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TOPICAL REVIEW

The Verwey transition—a topical review

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Online at stacks.iop.org/JPhysCM/14/R285**Abstract**

This review encompasses the story of the Verwey transition in magnetite over a period of about 90 years, from its discovery up to the present. Despite this long period of thorough investigation, the intricate multi-particle system Fe_3O_4 with its various magneto-electronic interactions is not completely understood, as yet—although considerable progress has been achieved, especially during the last two decades. It therefore appeared appropriate to subdivide this retrospect into three eras: (I) *from the detection of the effect to the Verwey model (1913–1947)*, being followed by a period of: (II) *checking, questioning and modification of Verwey's original concepts (1947–1979)*. Owing to prevailing under-estimation of the role of crystal preparation and quality control, this period is also characterized by a series of uncertainties and erroneous statements concerning the reaction order (one or two) and type of the transition (multi-stage or single stage). These latter problems, beyond others, could definitely be solved within era (III) (1979 to the present)—in favour of a *first-order, single-stage* transition near 125 K—on the basis of experimental and theoretical standards established in the course of a most inspiring conference organized in 1979 by Sir Nevill Mott in Cambridge and solely devoted to the present topic. Regarding the experimental field of further research, the remarkable efficiency of magnetic after-effect (MAE) spectroscopy as a sensitive probe for quality control and investigation of low-temperature ($4\text{ K} < T < T_v$) charge transport mechanisms is pointed out. Under theoretical aspects two concepts, going back to Mott and Ihle–Lorenz, presently appear most promising. Mott's view of the Verwey transition, as corresponding to the phase changing of a Wigner glass ($T > T_v$) into a Wigner crystal ($T < T_v$), describes most adequately the various low-temperature mechanisms in Fe_3O_4 in terms of tunnelling and variable range hopping of small polarons. On the other hand, the well-elaborated Ihle–Lorenz model, assuming a superposition of polaron-band and -hopping conductivity, is in better agreement with the high-temperature data ($T_v < T < 600\text{ K}$).

1. Introduction

A Verwey transition is classified today—in recognition of Verwey's pioneering work on the prototype of this class of transitions, first observed in magnetite (Fe_3O_4) [1, 2]—as the occurrence of a spontaneous, intercorrelated change of both lattice symmetry and electric conductivity in certain ionic crystals. Typically, such an abrupt change of crystallographic structure at a critical temperature, in Fe_3O_4 near $T_v \simeq 125$ K, is accompanied by further anomalies in a series of related parameters controlling the magnetic, thermodynamic, electric and mechanical interactions in the solid, see figure 1.

Verwey's original conception, comprising the experimental material up to the year 1947, proved to be formulated with such ingenuity that its basic statements could withstand the tempests of time. On the other hand, more detailed aspects of the original model—concerning, e.g. the *exact* crystal symmetry and *specific* type of ionic ordering in the low-temperature phase of Fe_3O_4 , the *precise* mechanisms of electronic charge transport within the various temperature ranges, the *accurate* microscopic interactions evoking the transition, etc—have been, since Verwey's first enunciations up to the present, under continuous discussion.

Moreover, the question as to which other transitions in alternative materials may—or may not—be of Verwey-type has been differently answered over the time, depending on the actual state of insight—as can be authentically followed, for instance, in the consecutive issues of Mott's fundamental work on *metal–insulator transitions* [3]. In view of these still existing irritations, the present report will focus on the original pilot material *magnetite* which, indubitably, is generally agreed to undergo a Verwey transition. Outlooks on related transitions in other compounds will be given only when of argumentative help for the discussion; such alternative transitions, also presumably of Verwey-type, have been thoroughly discussed in preceding reviews [3–8]. On account of the various still unanswered questions, even with respect to magnetite, however, confinement to the achievements obtained for the latter appears appropriate: sufficient comprehension of the *pilot system* (Fe_3O_4) is absolutely prerequisite in view of its application as a reliable reference for similar effects in related compounds¹.

Our present essay follows the historical path for passing in review the various conceptions developed over the years for an adequate description of the Verwey transition in *magnetite*, thereby referring with respect to the physical and chemical properties of ferrites, on corroborated standard textbooks [9–11]. In pursuing this conception, we found it useful to subdivide the 'magnetite story'—subsequent to the present short introduction (section 1)—into three eras: *era* (I) (section 2) covering the time of the first important experiments on magnetite which provided the basis on which, in 1947, Verwey was able to formulate his model. *Era* (II) (section 3) is devoted to the time between the inauguration of the Verwey model (1947) and the year 1979. The latter date is regarded as marking a milestone in the story of the Verwey transition, insofar as in this year Sir Nevill Mott arranged a stimulating conference in Cambridge under the topic 'The Verwey Transition' [4], which focused all experiences and data available at that time and gave impulse to future work. The lasting success of this conference has its sources in the unique personality of its host, Sir Nevill, who knew how to create an inspiring atmosphere in traditional Cambridge style, offering many chances to all participants for intensive discussions of their results and ideas—between the Cavendish Laboratory and Gonville and Caius College—which were often the initiation of continued interdisciplinary

¹ There exists unanimity today that, apart from Fe_3O_4 , in Ti_4O_7 [3] and Eu_3Si_4 [148b] charge order–disorder transitions of Verwey type are taking place. Initially, Mott also included in this group vanadium- $(\text{Na}_x\text{V}_2\text{O}_5, \text{Li}_x\text{V}_2\text{O}_5; 0.2 < x < 0.6)$ and molybdenum bronzes ($\text{K}_{0.3}\text{MoO}_3$) [3a]. A series of further compounds, undergoing metal–nonmetal transitions of possibly Verwey type, are discussed in some detail in the reviews of Honig [5], Brabers [7] and Imada [8].

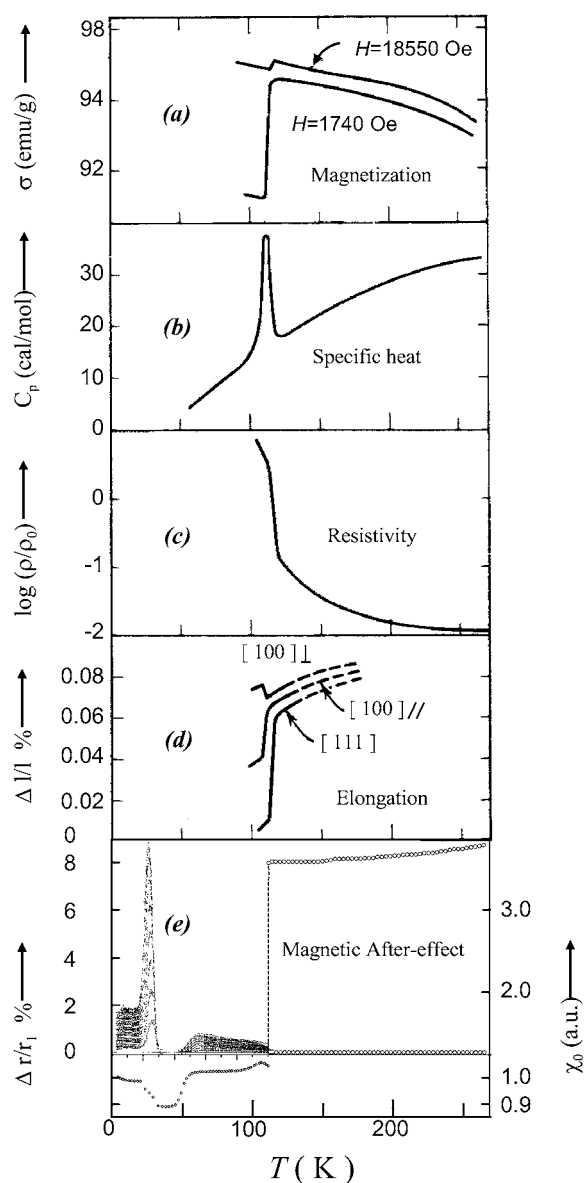


Figure 1. Basic manifestations of the Verwey transition in Fe_3O_4 near $T_V \simeq 125$ K, arranged in the historical order of their detection (cf [11]): (a) spontaneous jump of the magnetization [14]; (b) specific heat anomaly [21]; (c) spontaneous drop of specific resistivity [19]; (d) thermal expansion along selected directions [26]; (e) MAE spectrum, characterizing the low-temperature phase of perfect magnetite; the transition is indicated by the sudden decay of the relaxation at T_V in combination with a spontaneous jump of the initial susceptibility, χ_0 [185, 195].

cooperations under improved experimental and theoretical standards. *Era* (III) (section 4) embraces the ‘post-Cambridge era’ up to the present, trying to provide a survey on results and progress obtained since then in both the experimental and theoretical domains. Section 5, finally, is concerned with a summary of the actual state of insight into the Verwey transition and an attempt to gain an outlook on possible developments in the near future.

2. Verwey transition in Fe₃O₄—detection and first modelling

2.1. Early experiments in era (I) (1913–1947)

2.1.1. Magnetic measurements. Interestingly, a first indication of the Verwey transition in Fe₃O₄ was obtained as early as 1913 by the measurement of the initial susceptibility on a synthetic Fe₃O₄ polycrystal by Renger² [12, 13]. In addition to the then already well-known ferrimagnetic to paramagnetic order transition at 848 K, he detected an additional anomalous transition peak near 130 K. Later on, these initial results were supplemented by the investigations of Weiss and Forrer on the saturation magnetization of Fe₃O₄ [14] which they found to also undergo an anomalous spontaneous jump near 120 K. Detailed studies of this effect, as a function of magnetic field strength, revealed this anomaly to result—not from a variation of the magnetization itself, but—from a spontaneous induction of a large magnetocrystalline anisotropy, cf figure 1(a).

We find it worthwhile to mention, in this context, that the early measurements of Renger [12, 13] have pioneering character under two aspects: (i) he seems to be one of the first researchers to work with artificial³—instead of natural—magnetite which was the favoured material of most of his contemporaries, including Weiss and Forrer [14]. (ii) As measuring probe he used the initial susceptibility, a technique which our Stuttgart group developed decades later to an efficient instrument of magnetic after-effect (MAE) spectroscopy [15–17], by means of which we were able to contribute valuable results to the magnetite research, cf figure 1(e) and section 3.2.4(3). The magnetization studies of Weiss and Forrer were continued and qualitatively confirmed by Li [18] and Okamura [19] on natural single crystals, characterized by rather low critical temperatures of about $T_v \approx 113$ K. Li observed the effect of magnetic cooling, i.e. the freezing-in of the easy-magnetization direction along the $\langle 100 \rangle$ axis along which, on surpassing T_v , an external magnetic field had been applied. Additionally he noticed, on cooling, a reduction of the crystal symmetry from cubic to some type of uniaxial structure.

Extended investigations, during these early years, revealed that the observed variations of magnetic properties at T_v are only part of a fundamental transformation process in Fe₃O₄, giving rise to similar anomalies on a variety of other inter-related system parameters. Most of these effects are still under discussion to the present day, so that it may be interesting to shortly mention them in the temporal order of their detection.

2.1.2. Specific heat measurements. Anomalous specific heat maxima, occurring in natural single-crystalline magnetite at critical temperatures between 113 and 115 K, were reported by Okamura [19], Parks and Kelley [20], Millar [21] and summarized by Ellefson *et al* [22], cf figure 1(b). Surprisingly, all these early anomalous specific heat maxima are of single-peak structure—in contrast to many later measurements, revealing bifurcation (cf section 3)—although their relatively low peak temperatures identify these crystals as not being of highest perfection.

2.1.3. Electric resistivity measurements. These measurements, initially performed by Okamura [19] and Verwey [23], are characterized by a spontaneous jump of the resistivity

² These measurements were performed by Renger in the course of his thesis (1913), with Pierre Weiss and Albert Einstein (!) as advisors, at the ETH Zürich, Switzerland.

³ The motivation for the use of artificial magnetite was initiated by his measuring technique, which required specimens of toroidal shape with too large diameters ($d \approx 4$ cm) to be prepared from natural magnetite. Evidently, his production technique, based on the application of an oxy-hydrogen blow-pipe, yielded only rather imperfect magnetite, as may be deduced from its unusually high transition temperature of about 135 K, cf [167] and section 3.3.3 (footnote 9).

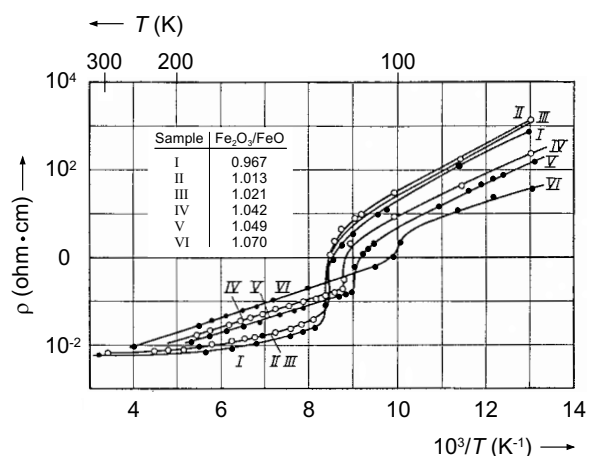


Figure 2. Verwey's original specific resistivity measurements on polycrystalline Fe₃O₄ bars, containing increasing amounts of octahedral vacancies, as indicated by the varying Fe₂O₃:FeO ratios of the inset [1].

by about a factor of 100 at the critical temperature T_v , cf figures 1(c), 2. In crucial experiments, Verwey and Haayman systematically investigated this jump height at the critical temperature as a function of the stoichiometry of carefully sintered polycrystals [1]. In proportion to excessive oxygen charging—thereby introducing octahedral vacancies into their specimens—they observed associated reductions of the jump amplitudes, together with a systematic lowering of the critical temperature from about 120 to 100 K, finally ending with the disappearance of the anomaly. As will be discussed in more detail later, the analysis of these results provided the basis for the formulation of the Verwey model.

2.1.4. X-ray analysis, thermal expansion. Early x-ray analyses failed to reveal any changes of the crystal structure, expected to occur at T_v in common with the other parameter variations [19, 22, 24]. These experiences were instructive for an estimation of the smallness of the actual lattice distortions which were confirmed dilatometrically by Okamura [19]. Later on, applying highly resolving strain-gauge techniques to synthetically produced Fe₃O₄ single crystals, Bickford was able to gain reliable expansion data along the basic crystal axes [25, 26], cf figure 1(d).

2.2. Verwey's transition model

In 1947 Verwey enunciated—as quintessence of the large body of experimental [12–14, 18–24] and theoretical [19, 27–30] results accumulated up to that time—the first consistent model concerning the peculiar temperature-dependence of a variety of system parameters in Fe₃O₄ [2, 30]. This model, though being of persuasive fascination concerning its conceptual baselines, has nevertheless offered, since its first formulation, a perpetual challenge for further refinement of some of its rather qualitatively formulated ideas. In order to have a firm reference frame with respect to our following considerations, it appears useful to outline briefly the basic conceptions of Verwey's original model.

Magnetite, since the early x-ray analyses of Bragg *et al* [31, 32] and Claassen [33] is known to crystallize in the spinel structure, specified generally as AB₂O₄, where two usually non-equivalent metal ions, A and B, are embedded in a cubically face-centred lattice of O²⁻ ions.

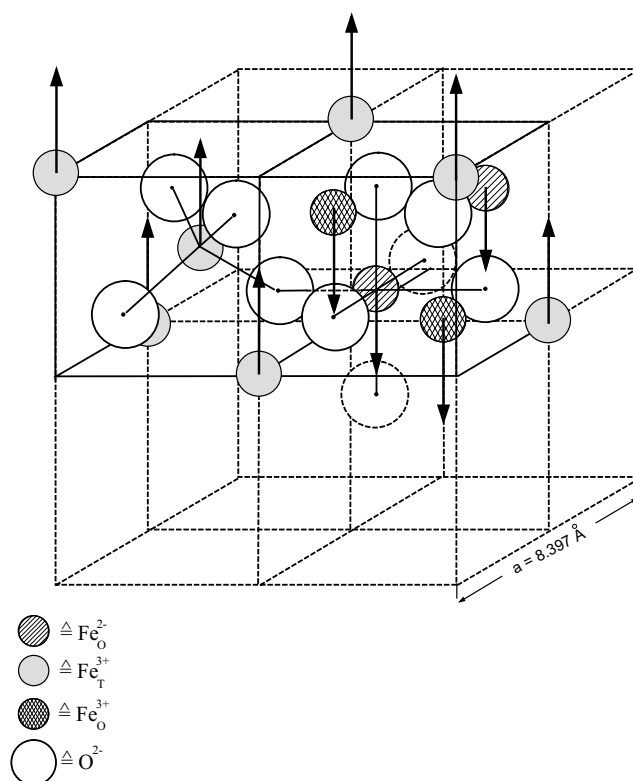


Figure 3. Lattice model of the inverse spinel Fe_3O_4 , cf [10], with the parameter of the unit cell, a , according to [37] and [7].

The unit cell of this lattice is composed of 32 closely packed O^{2-} ions embracing 64 tetrahedral (A-type) and 32 octahedral (B-type) interstices, cf figure 3. In normal spinels, only 1/8 of the A- and 1/2 of the B-type interstices are occupied by, respectively, eight divalent A- and 16 trivalent B-ions. During extended studies on semiconducting oxides, Verwey *et al* [23, 28–30] realized the relatively high conductivity of Fe_3O_4 above T_C ($10^3 < \sigma < 2.5 \times 10^4 \Omega^{-1}\text{m}^{-1}$) as compared to the rather low values ($\sim 10^{-5} \Omega^{-1}\text{m}^{-1}$) of normal spinels such as Co_3O_4 and Mn_3O_4 . From this striking difference they settled on an *inverse spinel structure* of magnetite—as Barth and Posnjak had done previously in the case of some related compounds [34]. Thus, they assumed a first octet of the 16 Fe^{3+} ions, constituting the unit cell, to be placed on eight A-sites, whereas the second octet, together with the remaining eight Fe^{2+} ions is distributed over the 16 B-sites. This way of lodging the two groups of differently valued Fe-ions on the given interstices, evidently supports electron exchange between equivalently B-sited, closely spaced Fe^{2+} and Fe^{3+} ions, according to the relation:



These general arguments in favour of an inverse spinel structure—being based especially on thorough x-ray [31–33] and conductivity [1, 2, 28–30] investigations—were further supported by the saturation magnetization of Fe_3O_4 , as determined by Weiss and Forrer [14] to 4.07 Bohr magnetons (μ_B) per formula unit. This value ($4 \mu_B$) is expected within the framework of Néel's concomitantly developed theory of ferrimagnetism [35], predicting antiferromagnetic coupling between A- and B-site located spins. In the case of an inverse Fe_3O_4 spinel structure,

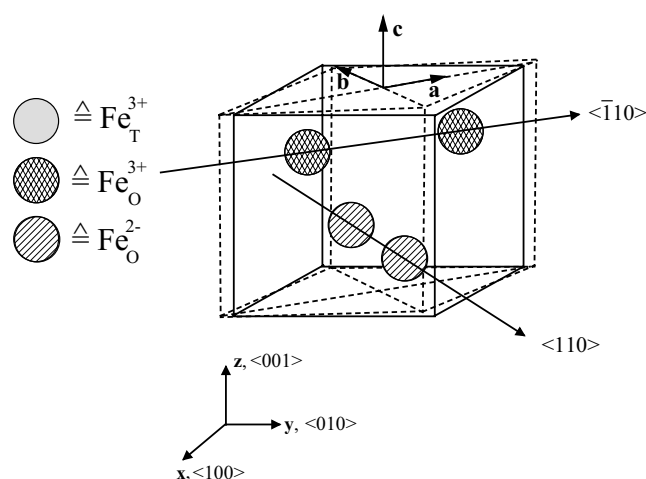


Figure 4. Illustration of the transition-induced orthorhombic deformation of Fe_3O_4 , according to [26], in combination with the one-dimensional ordering of Fe^{2+} and Fe^{3+} ions along the $\langle \bar{1}10 \rangle$ (*a*) and $\langle 110 \rangle$ (*b*) directions within alternating, $a/4$ spaced (001)-planes, as proposed by Verwey [2]; do not confuse the lattice parameter *a* (figure 3) with the direction vector *a* (*b*).

this means that the magnetic contributions of trivalent A- and B-type Fe^{3+} (d^5) ions are mutually compensated so that only spins of the B-sited Fe^{2+} (d^4) ions are contributing to the residual magnetization—according to Hund's rules and in agreement with experimental results [14]—of $2S = 2 * 2 = 4 \mu_B$ per formula unit, cf figures. The small experimental deviation from this value has been attributed to some residual orbital moment [35].

Once the inverse spinel structure of Fe_3O_4 had been established, it was only consequent to associate the spontaneous conductivity jump at $T_v \simeq 125$ K with an alteration of the electronic conductivity mechanism according to equation (1)—resulting, as only one specific facet, from the dramatic 'crash' occurring at T_v in the multiply intercorrelated many-component system called 'magnetite'. Thus, Verwey proposed the Fe^{2+} and Fe^{3+} ions, above T_v , to be randomly distributed over the B-sites, permitting relatively easy valency exchange according to equation (1) by means of thermally activated fast electron hopping. Upon cooling below the critical temperature ($T_v \simeq 125$ K), together with the reduction of the crystal symmetry from cubic [36] to tetragonal (as he originally assumed), charge ordering was proposed in a way that successive, $a/4$ -spaced (100) lattice planes would be occupied, alternatingly, by two- and three-fold Fe ions (cf figure 3). This ordering scheme is sketched in figure 4, showing two successive planes within which equivalent ions are aligned into chains, directed alternatingly in $\langle \bar{1}10 \rangle$ (*a*-) and $\langle 110 \rangle$ (*b*-) direction.

In formulating this magnetite model, Verwey was concerned to find interpretations of sufficient compatibility with the experimental material available at his time. Being convinced of the internal truth of his conceptions, he was wise enough not to insist on any *specific* type of ionic low-temperature ordering or on a *definite* crystal symmetry attained below T_v , but rather used the simplest interpretations available in order to formulate his ideas and to demonstrate their conformity with the stock of contemporary experiments [1, 2].

In a retrospective glance, one can state that this era of magnetite research (1913–1947) was characterized by a certain carelessness regarding the quality of the Fe_3O_4 crystals under investigation. Despite a basic knowledge of the high structure- and impurity-sensitivity of most physical properties of this complicated compound, most researchers used just that material

which was most readily available to them—frequently natural single crystals. No serious quality checks were usually undertaken, but the obtained results were nevertheless interpreted as being representative for perfect magnetite. In retrospect, this attitude may be excusable to a certain extent since reliable standards were lacking at that time—and even today the optimum analysing technique is still far from being common knowledge, cf section 3.2.4(3). On the other hand, owing to the varying quality of the crystals used by different searchers, many uncertainties and contradictions have been introduced into the field—some of which, even up to today, could not be completely eliminated as yet. During era (I) (1913–1947) and well into era (II) (1947–1979) a somewhat ‘mythic’ belief prevailed, regarding *natural* magnetite single crystals as an optimum material⁴ for systematic investigations despite the—already at that time—obvious fact that such crystals, depending on their origin, may widely vary in structure, stoichiometry, impurity content, stored stresses, etc [1, 2].

3. Verwey transition—era (II) (1947–1979)

3.1. Sphere of activities

With the formulation of the Verwey model, a wide field of research had been opened, inviting an abundant amount of experimental and theoretical investigations, all intended to prove and/or further refine the statements of the original conception. These efforts were concentrated mainly on the following central questions of increasing complexity: (i) crystal symmetry of the low-temperature phase; (ii) transformation characteristics—i.e. single- or multi-stage transition, first- or higher-order reaction kinetics; (iii) charge transport mechanisms above and below the critical temperature T_v ; (iv) ionic/electronic ordering schemes in the low-temperature phase.

Regarding the quality of the investigated crystals during era (II), the initially preferred natural material becomes gradually replaced by synthetically prepared single- and poly-crystals. This reflects the growing insight that, concerning the fabrication of perfect single crystals, ‘nature’ can in no respect compete with an accurately working metallurgist’s lab. On the other hand, even with such a lab, working on the basis of the detailed phase diagrams of Darken and Gurry [38], in addition to the recipes of Economos [39], it remains an art to produce really perfect single or poly-crystalline magnetite. The decisive condition for successful crystal growing consists in the perfect adjustment of oxygen partial pressure and temperature *during all fabrication steps* according to the phase equilibria rules for the system FeO–Fe₂O₃, cf section 4.1.1. By strict application of this strategy, Smiltens [40] was able to achieve a prime standard in the production of definite synthetic single Fe₃O₄ crystals. Later on Muan and Osborn [41] and Schmalzried *et al* [42] contributed detailed insights into the thermodynamic systematics, as documented in Muan and Osborns refined phase-diagram [41], cf figure 5. Crystal characterization during era (II), in the lack of generally accepted standards (cf section 4.1.1), is based only on rule-of-thumb estimations, if at all, i.e. regarding the transition temperature T_v (the closer T_v is to 125 K, the better the quality) and/or the acuity and height of the conductivity jump at T_v . Since, however, the crystal quality is of crucial importance for comparing and fairly judging the relevance of different experimental observations—especially with respect to their theoretical interpretations—the crystals discussed in the following shall be denoted, according to their

⁴ It is always with amusement that I remember the enthusiasm with which, some 25 years ago, a senior researcher supported our idea to combine, just for fun, a mountain tour into the Swiss Valais with the search for some natural magnetite single crystals, near Saas Fee and the famous Binn–Tal [14]. His enthusiasm even grew, when—after a successful mission—we were able to hand him some really nice looking crystals. I am not sure if he ever realized the poor quality we diagnosed, by means of MAE spectroscopy, for these crystals. Their spectra revealed the presence of nearly all possible types of lattice defects, in considerable concentrations: substitutional impurities, octahedral vacancies, internal stresses, etc, cf figure 18(a).

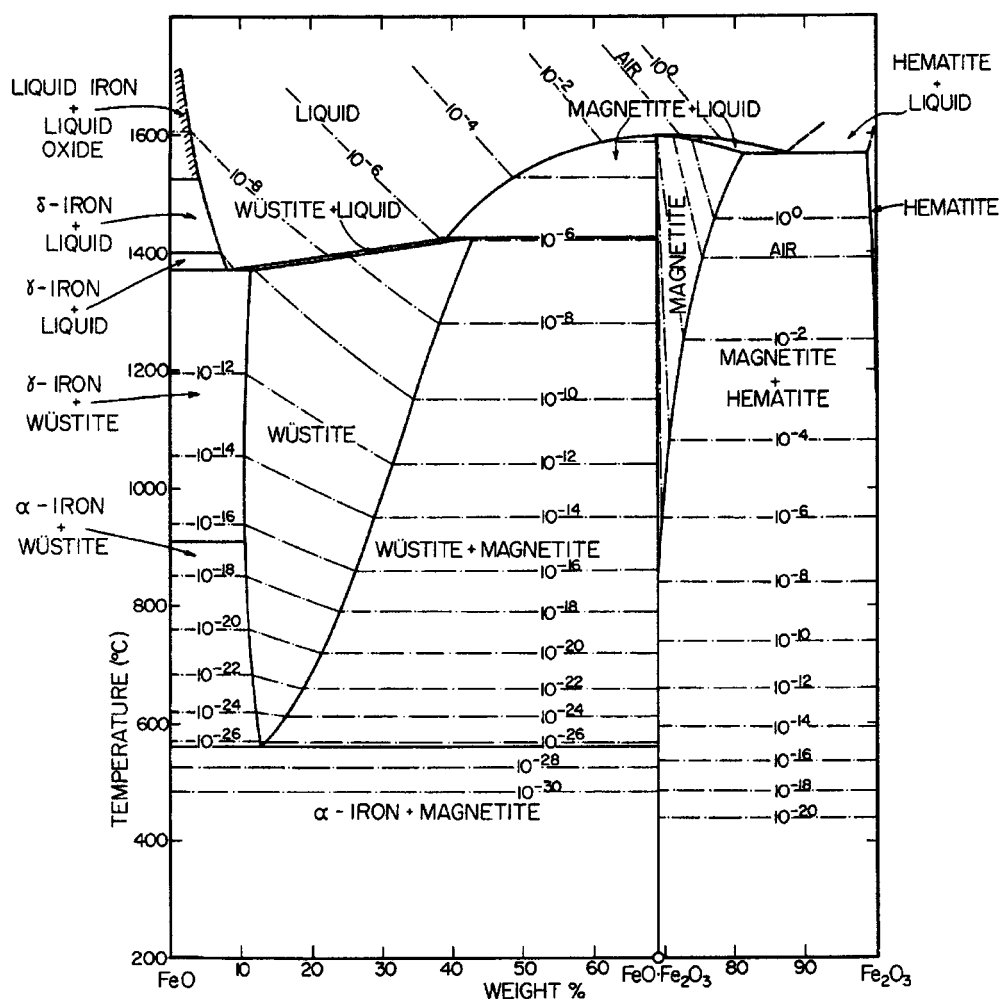


Figure 5. Phase relations of the system FeO-Fe₂O₃ [41], with heavy lines marking boundaries between respective phases and dash-dotted curves indicating oxygen isobars, indexed in atm units.

author's data, as follows: [NSC, T_v], [SSC, T_v] and [SPC, T_v] for natural single-, synthetic single- and synthetic poly-crystalline material, respectively, with T_v the relevant transition temperature. Especially, Smiltens-type synthetic crystals with, typically, $T_v \simeq 119.6$ K: [SSC, 119.6 K]—which were used in a series of early investigations—are abbreviated by SMIL.

3.2. Experiments in era (II) (1947–1979)

3.2.1. Crystallographic order. Whereas Verwey in his original model proposed tetragonal symmetry for the low-temperature phase of magnetite [2], Bickford immediately re-interpreted this, more precisely, to be of orthorhombic geometry [25]. This interpretation was generally regarded as appropriate for quite some time, even more so since this symmetry was supported not only by extensive anisotropy [26, 43] magnetization and conductivity investigations [44, 45], but, especially, also by x-ray [46] and, decisively, the neutron-diffraction studies of Hamilton [47]. These latter results were regarded as most reliable since Hamilton,

by carefully suppressing crystal twinning below T_v , had been able to clearly resolve a (002) reflection which was regarded as ultimate proof for an orthorhombic symmetry of the low-temperature Fe_3O_4 phase. This interpretation appeared even more conclusive since a variety of results [26, 43–47], all supporting this view, had been obtained on the same material of SMIL-type quality single-crystals.

First doubts were thrown on these Verwey-conforming views by the concomitantly performed x-ray analyses of Rooksby *et al* on *powderized* SMIL-type crystallites [48, 49], who deduced rhombohedral symmetry for the low-temperature phase of magnetite. In a careful consideration of the experimental material available at this time, however, Hamilton came to the conclusion that the powder x-ray results [48, 49] are of reduced relevance only as compared with the amount of other information—a view being similarly supported from later experiments, cf sections 3.2.2, 4.1.3—and that orthorhombic, or even lower, should be the more likely symmetry [46, 67].

Some few years later, diffraction studies by means of electrons (e^-) [SSC, 119.4 K] on thinned foils [50–53] and neutrons (n) [NSC, SSC \leq 118.5 K] [54] revealed half-integer satellite reflections, of the type $(h, k, l \pm 1/2)$, which pointed to a doubling of the lattice cell along the c -axis. Since such superlattice reflections are incompatible with the original Verwey model, they have been interpreted as indicating a more complicated low-temperature crystal structure than proposed by Verwey. These first questionings of the hitherto seemingly well established Verwey ordering initiated an avalanche of further studies, performed by means of all available techniques, which unanimously came to the conclusion that the original Verwey model had to be regarded as definitively disproved. Some of the most ambitious analyses supporting this view are collated in the following according to the various techniques applied: (i) electron [50–53]; (ii) neutron [54–59]; (iii) x-ray diffraction [60–62]; (iv) Mössbauer-effect (MOE) [63–71]; (v) nuclear magnetic resonance (NMR) [72–75]. The common tenor of all these various analyses may be summarized as follows:

- (i) The original Verwey ordering model, due to incompatibility with a majority of recent observations, has to be abandoned. Especially the superlattice reflections, revealed in e^- - and n -diffraction, point to non-Verwey-conforming unit-cell doubling. This is associated with frozen-in Δ_5 -mode charge density waves being induced during low-temperature condensation of phonon-coupled electrons [55, 56].
- (ii) The (002) reflections, originally observed by Hamilton and interpreted in favour of the Verwey model, are qualified by Shirane *et al* [57] as being of parasitic origin and—after elimination of perturbations—actually non-existent.
- (iii) The low-temperature crystal symmetry is identified as monoclinic, c_c , with a tendency to even lower symmetry when considering additionally minor deviations observed in magneto-electric experiments [76–78].

Some comments may be allowed at this juncture:

Plausible as these statements, formulated at the end of era (II), may sound, they, in turn, are not free of any ambiguity:

- (i) In none of all these numerous experiments was special care taken on the quality of the crystalline material—even worse, in some cases even the minimum crystal characterization [NSC/SSC, T_v] was lacking or given incompletely.
- (ii) Nevertheless, most researchers, completely blind vis-à-vis their unchecked material, were even fully ‘convinced that their results apply to *pure magnetite*’—thereby ignoring substantial insufficiencies clearly evident to the insider’s eye—as stated in [67], for instance, in view of data obtained on *natural* single crystals from *various* localities and undefined synthetic *powder*, cf section 4.1.3.

- (iii) On the other hand, an exemplary research strategy was early followed by Smiltens and his group, who were not only able to produce SSC of considerable quality [40] but, moreover, to also initiate detailed investigations on their material by generously offering it to colleagues working with different techniques [26,43–49]. This strategy had the advantage of eliminating *ab initio* all material uncertainties, arising usually when comparing results obtained on crystals of different provenance.
- (iv) On the other hand, however, it is only fair to state that even the crystals of Smiltens [SSC, 119.6 K]—like most crystals used in era (II)—were not of optimum quality. Instead of attaining, in terms of the ‘one-parameter-test’, best-values of $T_v \simeq 125$ K, they all were ranking in a lower class [SSC, <123 K]. However, frequently results obtained on crystals of SMIL-quality were questioned on the basis of information, deduced from crystals of lesser quality [50,54].
- (v) Evidently, owing to these uncertainties, resulting from (i) lack of perfect crystals and (ii) absence of reliable quality control, it would be unrealistic to expect the definite solution of the magnetite problem during era (II).

3.2.2. *Kinetics of the Verwey transition.* Two questions were dominating in this context:

(a) of what type is the Verwey transition—single-stage or multi-stage?; (b) of what reaction order are the observed single-stage or separated multi-stage transitions?

- (a) Multi-stage transitions in the neighbourhood of T_v have been reported from specific heat [79–84] and spontaneous magnetization in combination with Mössbauer-effect measurements [85–88]. Whereas in early specific heat investigations only one single anomaly, somewhat below 120 K, had been observed [19–22], later on the appearance of double peaks (pronounced bifurcation) near 113 and 119 K have been reported by Westrum *et al* [79–81] [NSC/SSC, ≤ 119 K], Matsui *et al* [82] [SSC, ≤ 118.4 K] and Rigo *et al* [83,84] [SSC, powder, 123 K]. For some time the phenomenon of a multi-stage-type Verwey transition has been under serious discussion, even more since Hirsch *et al* [85–88] [SPC, 116.6 K], too, promoted the idea of an extended multi-stage transition, composed of up to 12 stages within the temperature range $15 \text{ K} < T < 151 \text{ K}$ (!) [88]. Moreover, these multi-stage transition concepts were additionally supported by theoretical models developed by Cullen and Callen [89,90] and Chakraverty [91], cf section 4.1.

Interestingly, however, by careful consideration of the specific heat results of Matsui *et al* [82], all these erroneous multi-stage debates—with respect to perfect magnetite—could have already been concluded in 1977. Matsui *et al*, on carefully annealing their initially stress-deteriorated material, were able to completely eliminate the bifurcation and to raise the peak temperature, cf figure 6. From these results Matsui *et al* straightforwardly concluded that stress-released, stoichiometric magnetite is characterized by a *single-stage*, first-order Verwey transition as, in addition, they were able to convincingly demonstrate on a well-annealed single crystal, cf figure 6(d). Since, however, this well-verified finding [82] was not generally accepted, it took until the early 1990s before the ‘calorimetric bifurcation’ could be definitely revealed as an imperfection-induced effect and finally buried, cf section 4.1.3. On the other hand, the extreme multi-stage conception of Hirsch *et al* [85–88]—in view of their insufficient sample quality, which could be clearly identified by means of magnetic after-effect (MAE) spectroscopy [92], cf figure 18(b)—proved to be untenable and did not survive the 1979 Cambridge conference [4], cf section 4.1.2.

- (b) In era (II) there exists only a surprisingly small number of, even more, controversial interpretations concerning the *reaction-order* of the Verwey transition. Whereas in

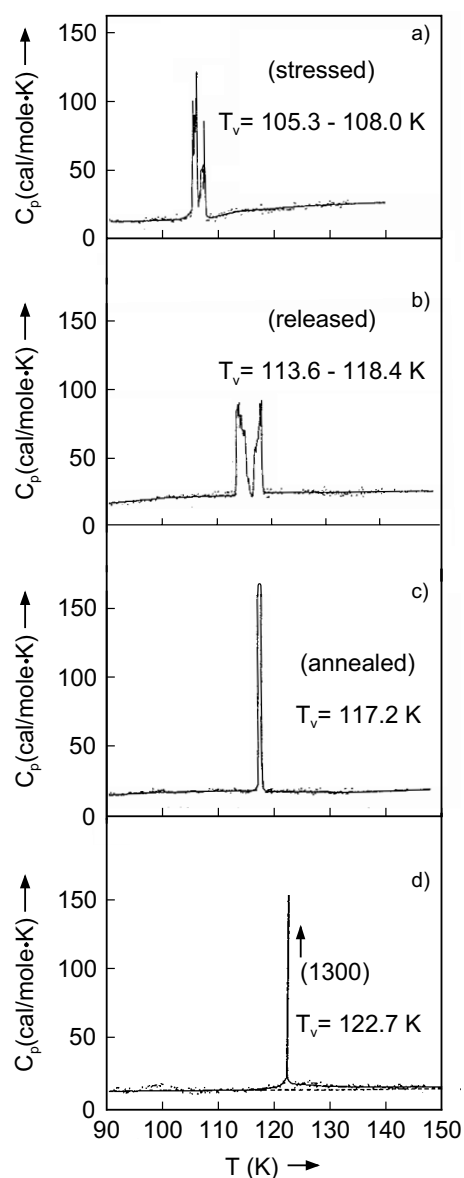


Figure 6. Influence of stress on the Verwey transition in Fe_3O_4 , as probed by means of the specific heat [82]: (a) polycrystalline specimen, containing preparation-induced *internal* stresses, exposed additionally to *external* stress; (b) specific heat after release of the external extra-stress; (c) specific heat after carefully annealing the specimen for ten days at 700°C ; (d) carefully prepared single crystal in thermal equilibrium.

Domenicali's view [44] second order should be dominant, Matsui *et al* [82], after careful sample-annealing, found the first order more adequate. In early theoretical models, too, the transition is alternatively described in terms of first [89,90] or second order [91].

Thus, at the end of era (II) the central questions concerning the transition mechanism—though being close to their solution—remained *de facto* still undecided.

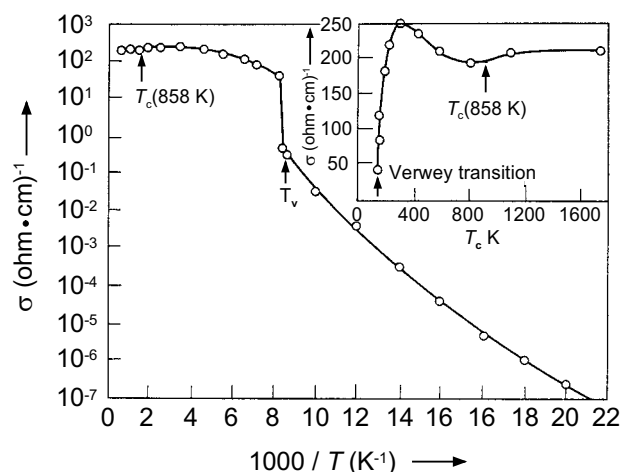


Figure 7. Typical temperature dependence of the electrical conductivity in Fe_3O_4 ; according to [93].

3.2.3. Charge transport.

(1) *Electrical conductivity.* dc conductivity measurement is probably one of the most frequently used techniques in the investigation of magnetite and related ferrites. This is due to the ease of performance and the considerable information deducible from such measurements. After the initial pilot studies [19, 23], Verwey *et al* were the first to systematically investigate the influence of intrinsic lattice defects—i.e. octahedral vacancies, induced by a small excess of $\gamma\text{-Fe}_2\text{O}_3$ during powder-sintering [1]—on the temperature (T_v) and the sharpness of the transition (figure 2). Since then, these two parameters, as determined by electric conductivity measurements, have usually served as an expedient gauge for judging the quality of magnetite crystals⁵ [44, 45, 93–100]. Beyond all these conductivity measurements, figure 7 may be regarded as a standard presentation, characterizing the typical information deducible from a moderate-quality Fe_3O_4 single crystal [SSC, 119 K] [93]. On further analysis one finds the conductivity to be thermally activated over the whole temperature range, with enthalpies increasing between 4.2 K and T_v from 0.03 to 0.15 eV, respectively, and reduced to a constant value of about 0.05 eV at (and above) T_v ; the positive temperature coefficient of σ within the range $T_v < T < 350$ K is incompatible with the assumption of a metal-like conductivity [10, 101, 102].

Electric conductivity measurements are especially helpful as sensitive indicators of *stationary variations* (see footnote 5) of charge transport mechanisms in the presence of *intrinsic* or *extrinsic* lattice defects. Intrinsic defects may be present due to (i) phase-rule violations during thermal specimen preparation [1], (ii) fast-particle (i.e. electron (e^-)) irradiation (section 4.2.3), (iii) application of stress either (a) unintentionally, e.g. during quenching at the end of thermal annealing or (b) intentionally, when studying the effect of hydrostatic pressure on the electric conductivity [103, 104], cf section 4.2.2. Extrinsic defects populate the lattice in the form of impurity atoms, introduced either during preparation due to imperfect source material or following definite impurity-doping in order to study their influence

⁵ Similar to electric conductivity, various other material parameters can be used as indicators for the detection of basic system variations (shift of T_v and acuity of transition) as shown, e.g. for the saturation magnetization by Myahara [105] by doping with a variety of impurity atoms.

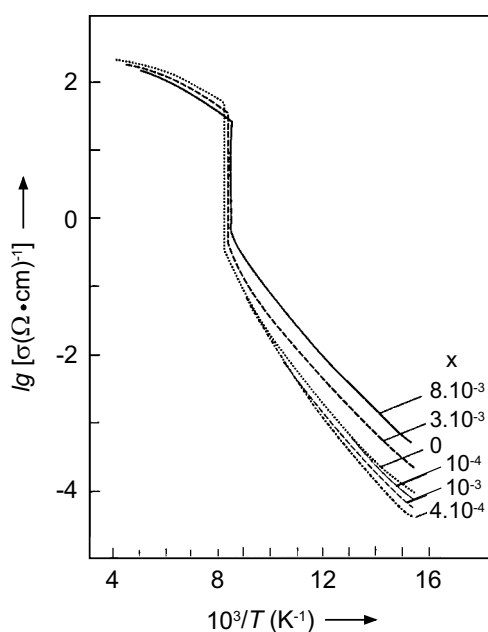


Figure 8. Typical influence of small amounts, x , of impurities (Ti^{4+}) on the electrical conductivity of magnetite: $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ [99].

on the material parameters of perfect crystals [93, 95, 99], cf figure 8. These effects, which played a decisive role in the conception of theoretical transition models, will be discussed in more detail later on (cf section 4.2.3).

(2) *Optical properties.* Attempts have been made to deduce additional information on the characteristics of the Verwey transition from investigations of the optical properties of Fe_3O_4 like reflection, refraction, absorption (optical conductivity), dielectric constants, etc [106–112]. Within the energy range $0.15 \text{ eV} < E < 0.8 \text{ eV}$, Buchenau *et al* [108] observed [NSC, $< 119 \text{ K}$] the optical absorption and dielectric constant to appreciably increase upon cooling down from 293 to 77 K and explained this effect in terms of a band model by pair-bonding polarons, cf section 3.3.3. On cooling powdered single crystals [SSC, $< 125 \text{ K}$] below T_v , Kuipers *et al* [110] observed drastic variations in the transmission spectrum ($0.025 \text{ eV} < E < 0.5 \text{ eV}$) of stoichiometric as opposed to Ti-doped ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$, $x > 0.1$) magnetite. Only for stoichiometric crystals, below T_v , were they able to resolve a splitting-up of two phonon bands at 0.0707 and 0.0472 eV into five sub-bands at, respectively, 0.0763 and 0.0726 eV, and 0.0521, 0.0503 and 0.046 eV. Optical absorption and reflectivity have been studied over wide ranges of photon energy ($0.03 \text{ eV} < E < 12 \text{ eV}$) and temperature ($50 \text{ K} < T < 320 \text{ K}$) using crystals of different types: (thin film: SSC, $\leq 199 \text{ K}$) [109], [NSC, $\leq 119 \text{ K}$] [111], [SSC, $\sim 125 \text{ K}$] [112]. In these photon absorption spectra only the low-energetic parts ($\leq 1 \text{ eV}$) may be associated with electric conductivity, whereas the higher energetic contributions result from wide-spread 3d-crystal field transitions [111, 112]. Optical conductivity near room temperature ($T > T_v$) is discussed in terms of small polaron models [109, 112], not without mentioning, however, that alternative band concepts according to Lorenz and Ihle may also lead to adequate descriptions [111], cf section 3.3.2.

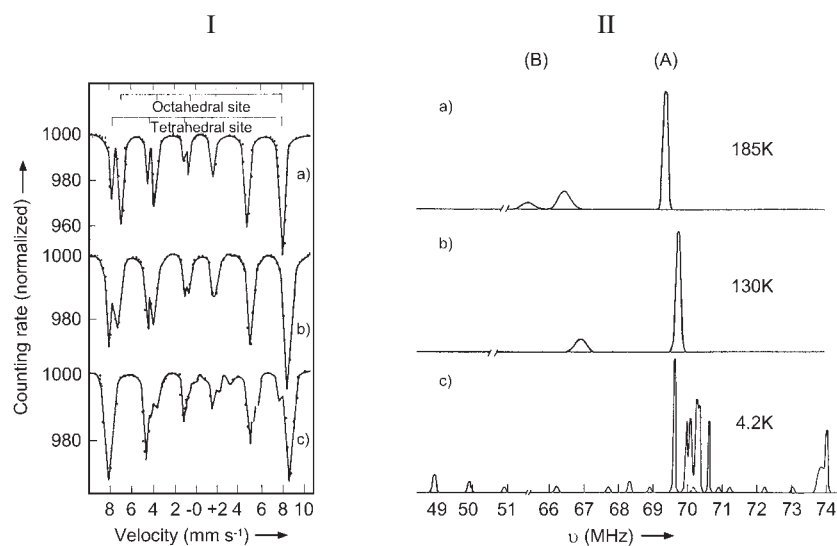


Figure 9. (I) Variation of the Mössbauer spectra of Fe₃O₄ on cooling across the Verwey transition: (a) 296 K, (b) 120 K, (c) 83 K [65]. (II) Variation of the NMR spectra of Fe₃O₄ on cooling across the Verwey transition: (a) 185 K, (b) 130 K, (c) 4.2 K [73]—with A and B denoting the lines of, respectively, A- and B-sited nuclei.

3.2.4. Low-temperature charge ordering. Of the techniques discussed so far, only electric conductivity measurements—on interpretation of their T_v -anomaly in terms of the Verwey model—are able to indirectly indicate charge ordering via carrier localization in the low-temperature phase of magnetite. Various other frequently used techniques during era (II) are able to provide even more direct information on transition-induced variations of charge transport mechanisms and thus were of great importance for theoretical model designing (cf section 3.3.3).

(1) Mössbauer-effect (MOE), nuclear magnetic resonance (NMR). These two techniques are treated under one heading, since they have in common a sensitivity not only to variations of stationary material properties (like e.g. the conventional electric resistivity technique) but also react, selectively, on alterations of dynamic system-parameters. Thus, their interesting feature consists of the drastic variations of their spectra when, on heating across the transition at T_v , the electron exchange frequency, ν_e , between the octahedrally-sited Fe ions (equation (1)), surpasses—in terms of the Verwey model—the Larmor frequency, of the order $\nu_L \lesssim 10^9$ s in MOE and NMR [113, 114]. According to this picture, the MOE and NMR spectra in the low-temperature range ($T < T_v$: $\nu_e < \nu_L$) are expected to be composed of three resonance lines—each one associated with one of the three different Fe-ions in the lattice, i.e. A-sited Fe³⁺ in addition to B-sited Fe²⁺ and Fe³⁺ ions. In the high-temperature range ($T > T_v$: $\nu_e > \nu_L$), however, due to ‘motional narrowing’, only two lines are expected—one induced, as before, from A-sited Fe³⁺ ions and the other reflecting the averaged contribution of rapidly exchanging Fe²⁺ and Fe³⁺ ions on B-sites. Whereas this latter two-line prediction proved to be correct for both resonance experiments (figure 9)—with the B-site component exceeding in strength and breadth, corresponding to the B/A site-occupation relation of 2:1 and ‘motional narrowing’ [65]—the low-temperature spectra were revealed, in both experiments, to be more intricately composed of a multiplicity of lines. In the case of MOE [63–71], these lines could

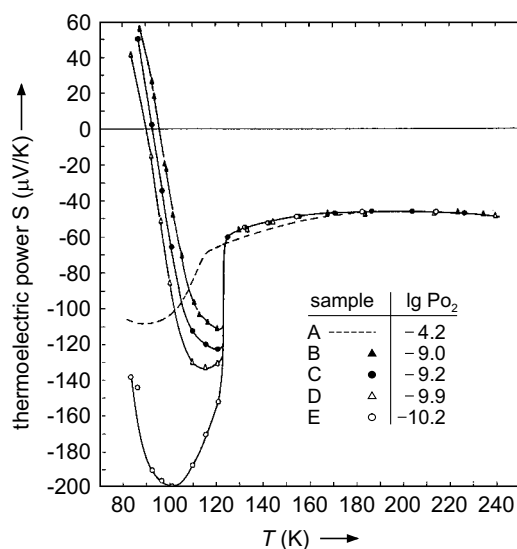


Figure 10. Variation of the thermopower on cooling across the Verwey transition [98]. Specimens A and E are supposed to be non-stoichiometric since they were tempered very close to the phase boundary (figure 5 [41]).

be resolved only numerically, yielding two doublets for the B-sited Fe^{2+} -, Fe^{3+} - and a singlet for the A-sited Fe^{3+} ions [NSC, 119 K] [66]. Following NMR [72–75], up to 24 distinctly separated lines could be observed at 4.2 K [73, 74]; [SSC, ≤ 123 K]. This multi-line splitting, on account of the thereby revealed further energetic differentiation of Fe^{2+} - and Fe^{3+} -ions, which originally were expected to fall into only three non-equivalent groups, was regarded as a serious argument against the initial Verwey model (cf section 3.3.3).

(2) *Thermoelectric measurements (TEM).* Contrary to low-temperature electronic conductivity, found to respond rather uniformly to impurities and other deviations from stoichiometry [93–99] (cf section 3.2.3), Hall-effect [115–118] and thermoelectric power measurements [98–100, 119] revealed transport of carriers of either negative or positive polarity. Whereas Hall-effect data, due to considerable difficulties in controlling the various experimental parameters—such as sample-purity, -stoichiometry, -geometry (thin layers) [117], -demagnetization, etc—frequently proved to be ambiguous, as comprehensively outlined in [7], thermopower results provided valuable insights into the conductivity mechanisms of magnetite [98, 100, 119]. On cooling, the thermopower (S) of perfect Fe_3O_4 undergoes at T_v (i) an acute decay from about -50 to $< -120 \mu\text{V K}^{-1}$ being followed, within the temperature range $125 \text{ K} > T > 80 \text{ K}$, by (ii) a retarded re-growth which, after sign reversal, attains values of up to $S > +50 \mu\text{V}$ [98, 119], cf figure 10. These effects have been associated with (i) spontaneous carrier reduction at T_v due to electron localization, being (ii) followed by a gradual change from n- to p-type carrier transport in proportion to a delayed establishment of ionic ordering in the crystal [98, 99]. According to this interpretation, thermopower results are most instructive since they contain information on both carrier localization and ionic ordering in the low-temperature phase of magnetite, cf section 3.2.4.

(3) *Magnetic after-effect spectroscopy (MAE)*. Of all the techniques currently available for the study of magnetically ordered systems, MAE is most sensitive in detecting tiny *variations* with respect to crystal structure, mobility of lattice defects and, in the case of ferrimagnetic materials, electron transfer according to equation (1) by giving rise to characteristically modified isochronal spectra, cf figures 1(e), 11, A.5. These spectra reflect the relaxation of the *initial susceptibility*, at given temperatures, due to decreasing domain wall mobility arising from time-dependent microstructural rearrangements of lattice defects or intra-atomic electronic states *within* the walls. All aspects of the MAE spectroscopy, concerning theoretical conceptions [15], technical realization [16] and practical application (study of atomic defects in α -iron and its alloys) [17], have been extensively described in the cited literature. The particular value of this high-sensitive technique for the study of conductivity mechanisms in Fe_3O_4 consists in the fact that only in the *low-temperature* phase, in contrast to the *high-temperature* phase, especially in single crystals of highest perfection, characteristic MAE spectra are induced—thereby indicating their basically intrinsic nature—which are extremely sensitive to any deviations from the perfect composition. Principally, these spectra owe their occurrence to the immediate coupling of inter-ionic electron exchange and local anisotropy transfer according to equation (1). Following this relation, anisotropic Fe^{2+} (with residual $3d^6: {}^5D_4$ momentum) are transformed into isotropic ($3d^5: {}^6S_{5/2}$) Fe^{3+} ions (and vice versa), thereby characteristically influencing—via modified interactions with the spontaneous magnetization—the domain-wall mobility. A further prerequisite for the observation of MAE spectra consists in a timescale compatibility between the electron exchange frequency ν_e and the observation times t_i , i.e. $\nu_e^{-1} \geq t_i \geq 1$ s. The fact that, upon cooling down, this latter condition is met only in the low-temperature phase, whereas in the high-temperature phase no MAE is observable (figure 11(c)), compares well with Verwey's prediction (and corresponding thermopower results (cf section 3.4.2)) assuming the transition at T_v to lead from a state of fast inter-ionic electron exchange ($T > T_v$) into a state of drastically reduced electron mobility for $T < T_v$, due to carrier localization.

In a series of early investigations [120–124] we analysed the influence of octahedral vacancies on the characteristic low-temperature spectra obtained on magnetite polycrystals prepared by either oxidation of high-purity iron strips or sintering analytically pure Fe_2O_3 powder under carefully controlled oxygen atmospheres according to the Fe_3O_4 phase diagram [41,42]. At the end of respective heat treatments, the specimens were rapidly quenched down to room temperature, thereby freezing-in (i) the equilibrium-dependent, expected content of B-site vacancies in addition, however, to (ii) unwanted internal stresses. This second effect was recognized to represent a severe handicap of the quenching technique, in addition to the fact that, inevitably, due to the short lag of phase-equilibrium during quenching, a small amount of additional B-site vacancies is introduced, cf sections 4.1.1, 4.1.3. (iii) Besides these intrinsic crystal defects, intended/unintended impurity atoms in the lattice are readily revealed and distinguished by means of characteristic variations in the low-temperature MAE spectra.

The influence of the various intrinsic and extrinsic lattice defects on the low-temperature MAE spectra of magnetite may be summarized as follows: (i) internal stresses give rise to the occurrence of anomalous relaxation spikes below T_v , controlling along their high-temperature flanks the delayed decrease (figure 11(a)) of a relaxation plateau which in perfect crystals extends monotonically within the range $50 \text{ K} < T < 125 \text{ K}$, ending with an abrupt decay at T_v , (figures 1(e) 11(c), 20(b)) [120–124]. (ii) Octahedral vacancies, corresponding to a relative increase of the oxygen content, δ , in the lattice ($\text{Fe}_{3-\delta}\text{O}_4$), cause a pronounced peak near 300 K, resulting from thermally activated jumps of Fe ions into these vacancies,

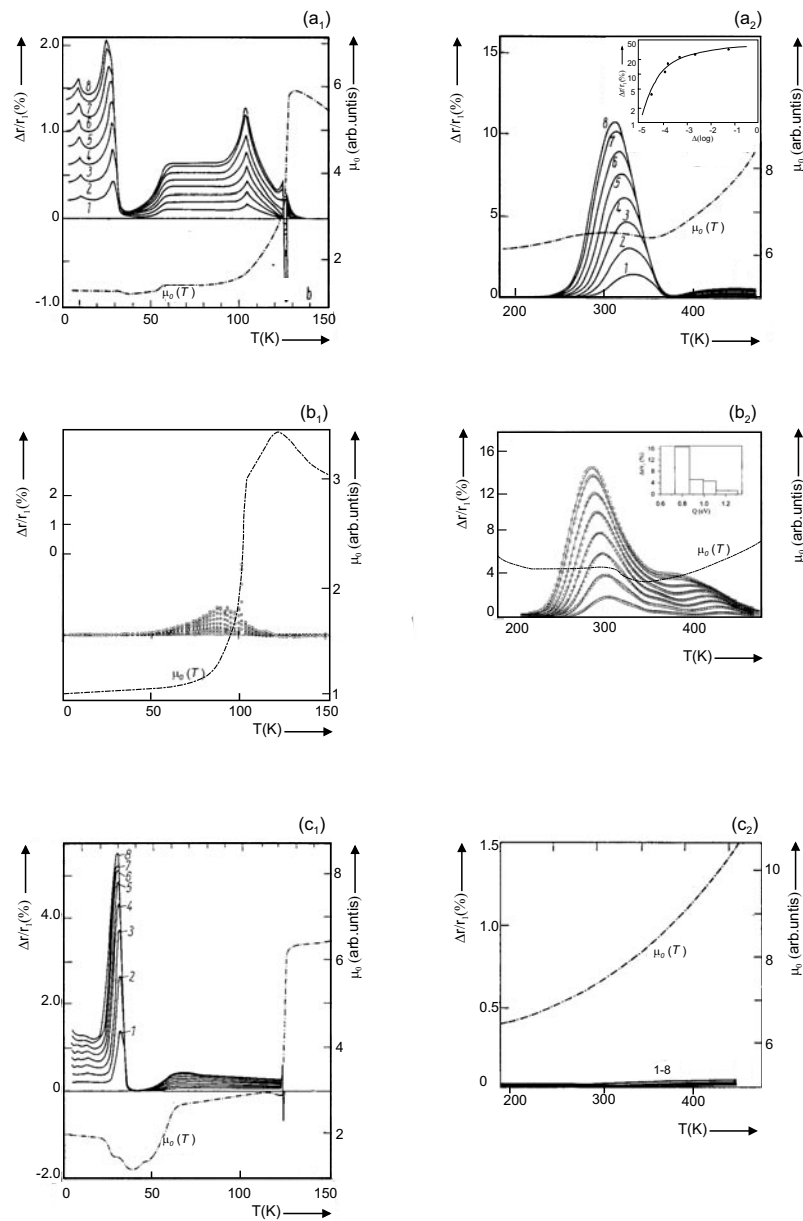


Figure 11. MAE spectra of poly- and single-crystalline Fe_3O_4 of various stoichiometry ($\text{Fe}_{3-x-\Delta}\text{O}_4$): (a) polycrystal revealing quench-induced deviations from perfect stoichiometry due to (i) internal stresses, as indicated by the relaxation spike near 105 K [121] and (ii) octahedral vacancies ($\Delta \simeq 10^{-4}$) giving rise to a characteristic Debye maximum near 300 K, whose strength as a function of Δ is shown in the inset of figure (a₂) [120, 185]; (b) polycrystalline, Mn-doped magnetite: $\text{Fe}_{3-x-\Delta}\text{O}_4$, with $x = 0.2$ and $\Delta \simeq 10^{-4}$ [212]; the inset of figure (b₂) shows the distribution of activation enthalpies contributing to the MAE spectrum; (c) ‘as-perfect’ Fe_3O_4 single crystal [185]. The isochronal relaxation of the initial reluctivity, $r(t)$, was measured—beginning at $t_1 = 1$ s after sample demagnetization—over the times $t_2 = 2$ s(1), 4 s(2), 8 s(3), 16 s(4), 32 s(5), 64 s(6), 128 s(7), 180 s(8) and plotted in the form $\Delta r/r(t_1) = [r(t_2) - r(t_1)]/r(t_1)$ [15–17]; the initial permeability μ_0 , like $\mu(t)$, depends on the susceptibility, $\chi(t)$, and the reluctivity, $r(t)$ via: $\mu - 1 \simeq \chi = 1/r$ (SI-system), cf the appendix.

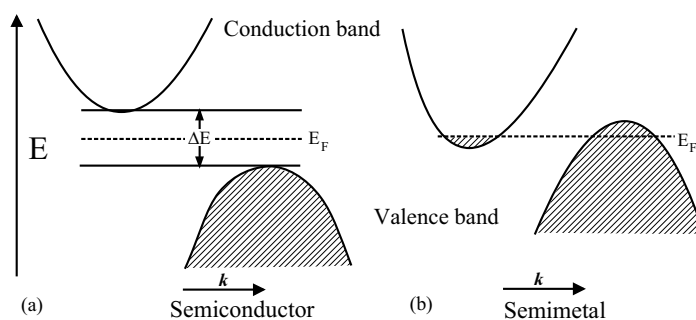


Figure 12. Illustration of a Wilson-type band-crossing insulator–metal transition: (a) insulating state of two separated bands with the Fermi-limit, E_F , lying within the band gap ΔE ($k \hat{=}$ wave number); (b) overlapping of the conduction and valence band as induced by, e.g., temperature- or pressure-variations, giving rise to metal-like behaviour (according to [127]).

figure 11(a₂) [120–124]. (iii) The additional presence of impurity atoms, of content x , in the lattice $\text{Fe}_{3-x-\delta}\text{O}_4$, is announced by the appearance of characteristic satellites, escorting the vacancy-induced 300 K peak at higher temperatures (figure 11(b₂)) [122]. All these various lattice perturbations (i)–(iii) have in common that, already at the lowest concentrations, they severely modify and finally suppress the lowest-temperature relaxation ($4.2 \text{ K} < T < 35 \text{ K}$). From systematic investigations of these effects (i)–(iii) in polycrystalline material, we obtained a body of valuable results and insights [120–125] which, upon extrapolation, enabled us to anticipate the MAE-spectrum of ‘ideal magnetite’ (cf figures 1(e), 11 (c), 20(b)) which, somewhat later, we were able to realize by means of ‘as-perfect’ single crystalline material, cf section 4.1.1.

3.3. Survey of theoretical models

In view of the kaleidoscope of diverging and sometimes even contradictory experimental results, sketched in the foregoing, it is not very surprising that, concerning the theoretical penetration of the field, only particular aspects were tackled without leading, as yet, to an all-encompassing view of the whole problem.

Thus, the spontaneous jump of the conductivity at T_v , since its detection, has been the most fascinating phenomenon inspiring numerous models concerned with low- and high-temperature electron transport mechanisms and, especially, the physical cause for their abrupt variation at the transition point. These considerations started with a series of models trying to explain how, under certain conditions, an electron ensemble may undergo an immediate change from a *delocalized* into a *localized* state. In view of the further discussion it appears useful to summarize these conceptions as follows.

3.3.1. Electron localization.

(1) *Wilson transition.* According to band theory a crystalline, divalent solid is of insulator-type if its Fermi level is located between a filled valence and an empty conduction band, both separated by an energy gap ΔE (figure 12(a)). According to Wilson [126], upon overlapping of the two bands—due to, e.g., variation of temperature or pressure—conduction sets in, thereby converting the solid from an insulator into a metal-type state (figure 12(b)).

As well described by Mott [127], Wilson's band theory of non-interacting electrons was regarded as authoritative for the treatment of metal–insulator characteristics, until about 1937 when the paradigmatic question arose why nickel oxide—despite an *unfilled* Ni²⁺ (3d⁸) *d*-band—instead of being a metal appeared as transparent insulator. Evidently, the early band theory was not aware, as yet, of a variety of possible interactions⁶ which, by band splitting [101, 128], are able to induce drastic variations of the system parameters. Thus, the insulating nature of NiO, after detection of its antiferromagnetism, was initially explained in terms of magnetic interactions giving rise to an e_g-band splitting into a completely filled lower and an empty higher sub-band, in addition to a completely filled t_{2g}-band of six spin-compensated electrons [129]. This explanation later became devaluated, however, by the fact that, upon heating across the Néel point (≥ 525 K), NiO did not change its insulator character. Henceforth, Coulomb interactions were regarded as the driving force for the persistence of the insulating state in NiO [3, 127]. It is to the credit of Wigner to have pointed out the fundamental role of Coulomb interactions for the localization of an electron gas [130].

(2) *Wigner transition.* According to Wigner's proposal, a 'jellium' at 0 K—i.e. an ensemble of free electrons, of density n , neutralized by a background of uniform positive charge—when steadily expanded, should finally crystallize into a non-conducting state (Wigner-crystallization). The condition of corresponding electron localization is obtained by minimizing the total energy of the electron gas, composed of kinetic and correlation energy, with respect to density, as follows (in CGS units):

$$\frac{1}{m} \left(\frac{\hbar}{e} \right)^2 n^{1/3} = a_{\text{H}} n^{1/3} = \text{const} \quad (2)$$

where a_{H} is the hydrogen radius and the constant estimated to be about 0.05 [3].

(3) *Mott transition.* Mott considered a linear crystalline array of one-electron atoms at zero temperature with steadily tunable lattice constant a . For small a , due to correlation, the electrons of the corresponding half-filled valence band are delocalized and characterized by metal-like mobility. With increasing a , the band is continuously narrowed, finally ending in the discrete levels of the individual atoms, cf figure 13. In this extreme case of electrons localized at their respective atoms, the system is converted into an antiferromagnetic insulator—in spite of its still half-filled valence band.

Extending these considerations to three dimensions yields the following relation for the critical density, n , initiating the metal–insulator transition of the system [3, 131]:

$$\varepsilon_r \frac{1}{m} \left(\frac{\hbar}{e} \right)^2 n^{1/3} = \varepsilon_r a_{\text{H}} n^{1/3} \simeq 0.25 \quad (3)$$

with ε_r the background dielectric constant and a_{H} , as in (2), the hydrogen radius. Condition (3), by its prediction of electron localization, defines the limits of band conduction in the case of narrow bands. Moreover, this Mott transition describes a first-order process due to the implicit accounting of carrier-dependent (n) screening of electron–hole pair interactions which, at elevated temperatures, for a certain n become instantaneously destabilized [132].

⁶ Further possible interactions, besides electron correlation, leading to electron localization by extra-splitting of the level system, are extensively discussed by Adler [101, 128] in terms of: (i) changes of crystal symmetry, due to lattice distortions, causing doubling of the unit cell; (ii) *d*-band splitting in the presence of an antiferromagnetic lattice; (iii) electron–phonon interactions.

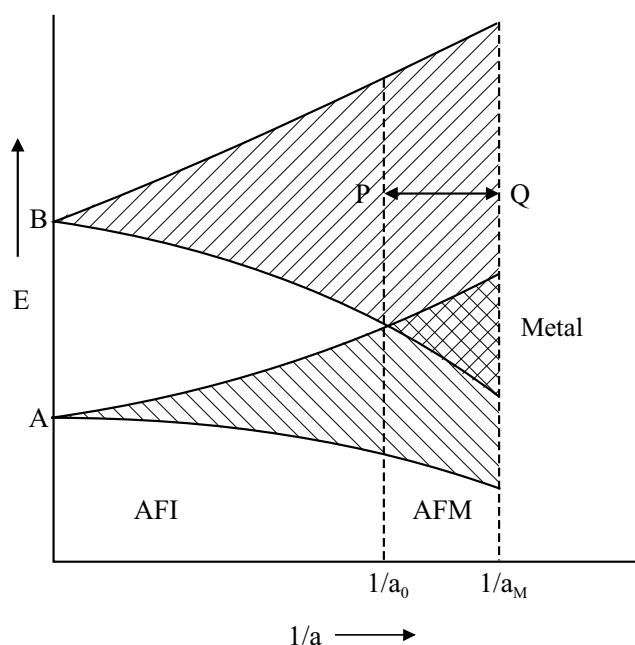


Figure 13. Energy distribution within two Hubbard bands as a function of the distance, a , of their respective atomic centres: AFI = antiferromagnetic insulator, AFM = antiferromagnetic metal; a_0 = setting-in of metal–insulator transition; a_M = disappearance of antiferromagnetic order [3].

(4) *Hubbard–Mott transition.* Whereas electron correlation is accounted for only rather qualitatively in the transition models of Wigner and Mott, Hubbard was the first to introduce explicitly a correlation term into the Hamiltonian for band-conductivity calculations. He found simulation of a metal–insulator transition to be successful by introducing only an *intra*-atomic correlation term, $U = \langle e^2/r_{12} \rangle$, without further consideration of any long-range Coulomb interactions. Thus, in terms of the Wannier formulation, he proposed the following Hamiltonian [133, 135]:

$$H = \sum_{ik\sigma} T_{ik} c_{i\sigma}^+ c_{k\sigma} + U \sum_i n_{i\sigma} n_{i-\sigma} \quad (4)$$

using the following notations: T_{ik} nearest-neighbour hopping integral expressible by $B/2z$, with B the bandwidth and z the coordination number, c^+ and c the particle creation and annihilation operators, σ the spin direction and $n_{i\sigma}$, $n_{i-\sigma}$ the electron number operators. Hubbard showed that application of the Hamiltonian (4) on an array of one-electron atoms yields two split bands (cf figure 13) which start to overlap for $a < a_0$ – a condition met, according to his analysis, for $B/U \geq 1.15$ (cf figure 14). As indicated in figure 14, the Hubbard approximation is able to reproduce the whole range of behaviour: from band conduction to the localized insulator state.

(5) *Anderson localization and transition.* Anderson, in studying the influence of disorder on the mobility of non-interacting electrons discovered, above a certain limit, the setting-in of a disorder-induced spatial localization of electrons. In order to allow a quantitative treatment, disorder is formalized in terms of certain random fields, as shown in figures 15(a), (b) where a crystalline array of potential wells is superimposed by a random potential V , varying between

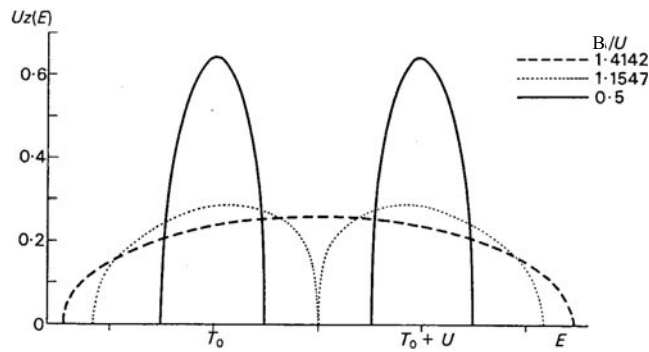


Figure 14. Band splitting due to electron–electron interactions in terms of the Hubbard model [133]: U = effective Coulomb repulsion of two electrons within the same ion; $z(E)$ = density of states; B = bandwidth.

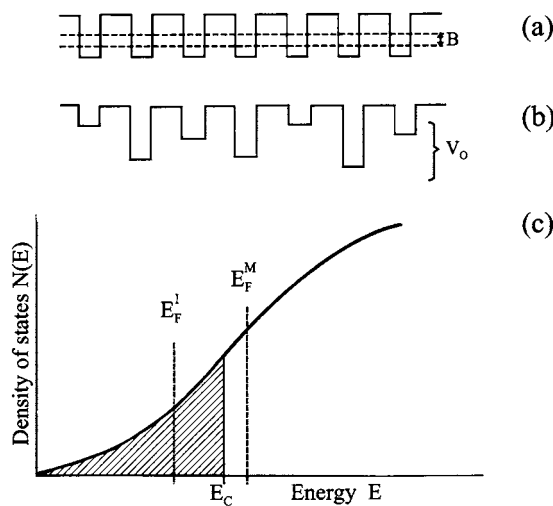


Figure 15. (a) Periodic potential of the unperturbed lattice; (b) superposition of a random potential ($\pm V_0/2$) on (a) with $V_0 > B$; (c) density of states in a non-crystalline solid with a mobility edge, E_C . Depending on the relative localization of the Fermi-energy, E_F , the material behaves as a metal-like conductor ($E_F^M > E_C$) or as an insulator ($E_F^I < E_C$) [3].

the limits $\pm 1/2V_0$. In order to perform a three-dimensional tight-binding approximation, Anderson defined the Wannier-compatible Hamiltonian [134, 135]:

$$H = \sum_{ik} Q_{ik} c_i^+ c_k + \sum_i E_i n_i \tag{5}$$

with c_i^+ , c_k and n_i denoting, as in (4), particle generator-, annihilation- and number-operators, respectively. The first term, governed by the hopping energy Q_{ik} , describes the transition probability between two neighbouring sites; the energy E_i of an electron in site i —whilst being constant for all sites, $U_i = U_0$, in a perfect solid—due to the random field varies here within the range $(U_0 - V_0/2) \leq U_i \leq (U_0 + V_0/2)$.

The Anderson treatment leads to a criterion for electron localization as a function of the random-field strength, V_0 , in relation to the bandwidth, B [3, 134, 135]:

$$V_0/B > c \quad (1.4 < c < 2.7) \tag{6}$$

where the limit c is found to vary somewhat with the specific assumptions entering into the calculation [3, 135]. The essential result of (6), however, is the prediction that beyond a certain degree of disorder, an electron gas will transform into a localized state, denoted by Anderson as a ‘Fermi glass’.

As pointed out by Mott [3], for $V_0/B < c$, the Anderson model describes a situation where high-sensitive electrons near a band end are localized already, up to an energy $E \leq E_C$, whereas electrons with $E > E_C$ remain delocalized and contribute to the conductivity (cf figure 15(c)). In this case of partial localization, the position of the Fermi energy E_F relative to the so-called mobility edge, E_C , decides whether the solid is of insulator ($E_F \leq E_C$) or ‘metallic’ conductor type. A conductivity change (Anderson transition) is induced if, by any event, a reversal of the relative sequence of E_F and E_C is induced by either a shift of E_F (variation of the electron number) or E_C (structural change of the solid).

3.3.2. Electron transport mechanisms. With the aforementioned models in mind, it appears useful to briefly distinguish between the basic mechanisms of electron transport discussed with regard to the temperature-dependent conductivity of Fe_3O_4 :

- (1) *Band conduction* of delocalized electrons ($E_F > E_C$)— also sometimes denoted, too globally, as metallic conduction. Metallic conduction in the true sense, however, is characterized by an absence of thermal activation and a positive temperature coefficient of the resistivity, as opposed to a negative one, characterizing e.g. intrinsic semiconductors, cf section 3.2.3.
- (2) Thermally activated *hopping* of localized electrons residing, in terms of the Anderson picture, below the mobility edge. On account of their charge, such hopping may be accompanied, in polarized solids, by a ‘cloud’ of lattice deformation, following the electron during its migration through the lattice. This combination of electron and polarization-induced strain field may be treated as a quasi-particle called a ‘polaron’. Evidently, from the classical point of view such polaron migration can be regarded as migration of an electron with reduced mobility due to an increased effective mass m^* , whereas in the particle picture these same electron–lattice interactions are interpreted in terms of *electron–phonon* processes.
- (3) Polaron transport *mechanisms*, with special regard to transition metal oxides, may be distinguished with respect to the type of engaged polarons [135–142], i.e. *large* or *small*, which are usually characterized by two parameters: a dimensionless coupling constant, α , and the polaron radius, ρ , containing the influence of both lattice deformation, U_L , and phonon energy, U_P [135]:

$$\alpha \sim \frac{U_L}{U_P} \quad (7a)$$

$$\rho \simeq \sqrt{\frac{\hbar\omega_L}{2m^*\omega_L^2}} \quad (7b)$$

with, in (7b), $\hbar\omega_L$ the maximum energy of longitudinal optical phonons and the denominator corresponding to the elastic response of the lattice. Evidently, these two parameters are reciprocal to each other so that small coupling ($\alpha \ll 1$) corresponds to large polaron radii ($\rho \sim 10$ – 100 lattice constants), whereas strong coupling leads to small polaron (SP) radii approaching, in the limit, the lattice constant. The latter case corresponds to an extremely increased effective mass, m^* , and correspondingly reduced mobility of the electron, ending in its localization.

Polaron transport has to be considered within the two temperature ranges (i) $T > T_0$ ($T_0 \rightarrow 0$ K) and (ii) $T \leq T_0$ —of which the former may be further subdivided into $T_0 < T \leq T_v$ and $T_v < T$. In terms of band-conduction, for $T > T_0$, polaron bands may principally exist, thus permitting charge transport by means of intra-band conduction and, eventually, off- (or inter-) band hopping. In the case of narrow or disturbed (e.g. by impurities) polaron bands, hopping mechanisms are supposed to prevail in the form of (i) intra- and (ii) inter-band hopping. In the second temperature range ($T \rightarrow 0$ K) small-polaron states are expected to form narrow bands of temperature-dependent width [135]. Within these bands—if undisturbed by any defects—unactivated charge transport in the form of *coherent tunnelling* is feasible. In view of the *MAE spectroscopy*, it is important to note that domain-walls—as locations of increased magnetocrystalline interactions, evoked by the internal rotation of the magnetization vector—may be regarded as perturbed lattice zones within which electronic charge exchange may be enabled by *incoherent tunnelling*, i.e. tunnelling assisted by thermally activated adjustment of levels [143]. Upon slightly increasing temperatures, however, such bands become rapidly narrowed, thereby causing localization of small polarons and thus restriction of charge transport on hopping processes only [140].

- (4) *Bipolarons* have been proposed to result spontaneously from the attraction of polarons at lower temperatures, thereby inducing corresponding reduction of the electrical conductivity [144–146]. Such attractions are feasible to arise in the case of strong electron–phonon coupling if the relative energy gain, due to the bipolaron-induced local lattice deformation, is greater than the Coulomb-repulsion [3, 145].
- (5) *Anderson’s condition* was formulated in view of some peculiarities connected with the Verwey transition of magnetite [147]:
 - (i) the relatively low transition temperature of $T_v \simeq 125$ K;
 - (ii) the thermal activation of conduction, persisting—despite a relatively high, quasi metal-like conductivity—within the temperature range above T_v ($Q \simeq 0.05$ eV) [10, 101, 102], cf section 3.2.3(1).

Using a Madelung approximation, Anderson estimated the energy difference between perfect Verwey order and complete disorder to amount to about 2–3 eV so that a corresponding transition would be expected only for temperatures $> 2 \times 10^4$ K. In order to explain the lower temperature of only $T_v \simeq 125$ K, he assumed the actual transition to be less rigorous and occurring only between two alternate order states, of long-range order (LRO) and short-range order (SRO) types. The assumed residual SRO state above T_v is in agreement with both (i) the occurrence of thermally activated conductivity for $T > T_v$ and (ii) the concordance between the observed transition-induced molar entropy variation of about 0.3 R (cf section 4.1.3) with the predicted value of 0.2 R for a LRO–SRO transition, as opposed to $\Delta S = 0.69$ R, expected for a complete order–disorder transition at T_v [147, 148].

The Anderson SRO is characterized as a state of minimum lattice energy, realized by a maximum number of adjacent, octahedrally sited Fe^{2+} – Fe^{3+} pairs, cf figure 16. In this arrangement all B-type tetrahedra, always sharing one corner with one another, are occupied by two Fe^{2+} and Fe^{3+} ions, thus carrying a charge of $5e^+$ per tetrahedron⁷. As outlined by Anderson, there exists an infinite number of ionic configurations meeting these conditions which thus, in terms of nearest-neighbour interactions, all possess the same energy hence

⁷ Another useful way to describe Anderson’s short-range order is in terms of hexagons always sharing, as depicted in figure 16, one corner with one tetrahedron, thereby obeying the model-specific ionic (2+) to (3+) alternation. As may be imagined, cf position I, each B-site is shared by six hexagons, thus leading to a coordination of, i.e. $(1/6 * 6 = 1)$, one B-site to one hexagon.

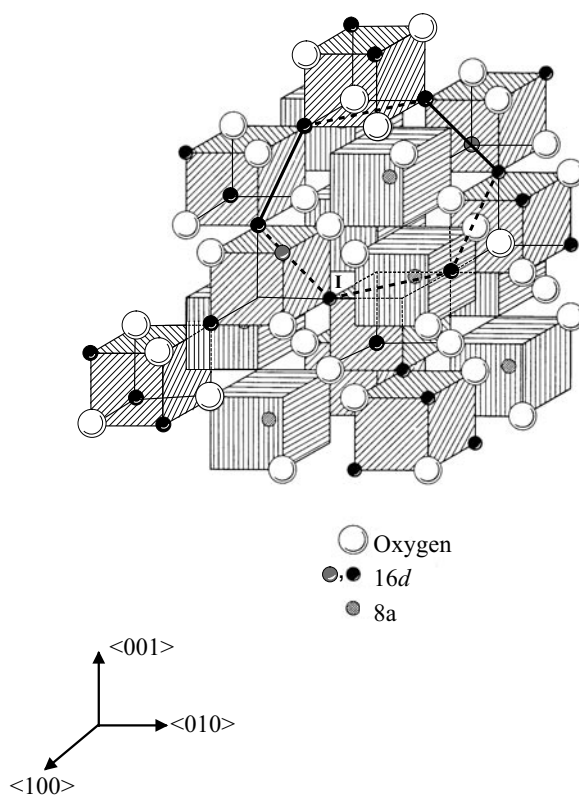


Figure 16. Illustration of the Anderson condition within the inverse spinel lattice of Fe_3O_4 (in order to improve the transparency, some of the $B(d)$ -type occupied cubes have been ‘opened’; $B(d)$ -type Fe ions which only in the chosen projection, seemingly, lie on the hexagon have been marked by a less intense black colour). This figure may help to visualize various aspects of the Anderson conception: (i) the B-type tetrahedra, occupied by pairs of Fe^{2+} and Fe^{3+} ions; (ii) the hexagons formed of alternating Fe^{2+} and Fe^{3+} ions always belonging, respectively, to one of six adjoining tetraheders; (iii) the intersection of six hexagons in one B-sited Fe-ion, i.e. in position I (cf [11]).

forming an infinitely degenerate, ‘frustrated’ ground state. In terms of this model, LRO—of e.g. Verwey-type—cannot be achieved by means of nearest-neighbour interactions alone but, possibly, in the presence of additional interactions, like e.g. next nearest Coulomb attractions.

3.3.3. Conceptual extensions of the Verwey model (era II). Based on the rich—though not always unambiguous—experimental material, various attempts were made to develop all-embracing theoretical conceptions, surpassing the original Verwey model, in order to master the intricate magnetite problem:

(1) *Polaron-based models.* Haubenreisser [149], followed by others [112, 150–153], was the first to treat quantitatively the problem of high-temperature ($T > T_v$) conductivity in Fe_3O_4 , using a hopping model of *non-interacting* polarons. This attempt, allowing to reproduce the occurrence of the experimentally observed high-temperature conductivity maximum [149] revealed, nevertheless, some insufficiencies of the chosen model since the correct location (~ 300 K, cf figure 7) was missed by a factor of two (600 K). Similarly, Šimša [112], when calculating the room temperature conductivity of Fe_3O_4 in terms of a non-interacting SP model, obtained a value too small by a factor of 5, of only $55 \Omega^{-1} \text{cm}^{-1}$ (cf figure 7). In order to

overcome these handicaps, Klinger *et al* [141, 142] proposed a two-phase model predicting in the low-temperature range ($T < T_v$) a state of strongly *correlated* polarons which, upon a first-order transition at T_v , attain for $T > T_v$ a state of high disorder with only some remaining, residual correlation. This model was elaborated to a level allowing order-of-magnitude estimates of conductivity phenomena in Fe_3O_4 .

Another proposal, due to Chakraverty [91], attributed the low-temperature Verwey ordering to a cooperative Jahn–Teller transition, thereby directly inter-connecting the variations of crystal structure and conductivity, the latter being characterized by localization ($T < T_v$) and hopping ($T > T_v$) of polarons. The here assumed Jahn–Teller distortion, however, remained without experimental verification [138]. As an ultimate mode of polaron transport, accounting for polaron–polaron interactions, the formation of *bipolarons* has been suggested. In view of the successful application of this model on related conductivity transitions in Ti_4O_7 [144, 154]⁸ and Yamada’s concept of ‘molecular polarons’, deduced from diffuse neutron scattering [56], Chakraverty suggested to analogously associate the Verwey transition in Fe_3O_4 with bipolarons [145]. Thereby, bipolarons and molecular polarons are regarded as synonymous polaron configurations, resulting from attractive, elastic interactions between two localized electrons. In this picture, the drastic conductivity change at the Verwey transition is due to the transformation of an ordered low-temperature phase ($T < T_v$) of correlated bipolarons into a high-temperature phase of disordered bipolarons. Thermal dissociation of these latter with increasing temperature, in the range $T > T_v$, explains the moderate conductivity growth up to about 300 K (cf figure 7).

(2) *Band-based models.* Cullen and Callen [156] proposed band conductivity to be the dominant charge transport mechanism in Fe_3O_4 by assuming the two B-sited Fe-ions (per formula unit) to distribute their 11 d-electrons, as a function of the spin-state, on two distinctly separated bands. In this picture, according to Camphausen *et al* [153], the lower-energy band is completely filled by ten electrons of, e.g. spin-down orientation, whereas the eleventh, spin-up electron solely occupies the higher-energy band, thus initiating metallic conductivity above T_v . Cullen and Callen formulated the problem in terms of a Hubbard-like Hamiltonian, cf equation (4) [90, 156, 157]:

$$H = \sum_{i\alpha,k\beta} T_{i\alpha,k\beta} c_{i\alpha}^+ c_{k\beta} + \sum_{i\alpha,k\beta} U_{i\alpha,k\beta} n_{i\alpha} n_{k\beta} \quad (8)$$

where $U_{i\alpha,k\beta}$ denotes the *inter-atomic* Coulomb interactions of neighbouring ions, positioned on B-type lattice sites (i, k) of adjoining tetraheders (α, β); spin-summation is cancelled in view of the singlet state of participating electrons; the other symbols correspond to those of equation (4). Hartree–Fock approximations, based on Hamiltonian (8), indicate electron-localization for relations $U/B \geq 3 - U$ and B denoting the effective Coulomb potential and bandwith, as related to U_{ik} and T_{ik} , respectively. Thereby, reaction order one is predicted for the transition into the localized state, whereas for $U/B < 3$ multiple ordering is expected [90, 156]—a result most welcomed at its time, since it facilitated the interpretation of atypical transitions observed in imperfect Fe_3O_4 crystals. Sokoloff [158, 159]

⁸ The bipolaron model has proven an adequate means for explaining the *two* transitions occurring in Ti_4O_7 : on heating up, a first lower-temperature transition near 130 K leads to a conductivity increase of about a factor of 10^2 , without changing the diamagnetism of the semiconducting material. Upon a second transition near 150 K, the conductivity jumps again by a factor $> 10^2$ and the material becomes paramagnetic. These observations are explained in terms of a structured low-temperature order of diamagnetically bound Ti^{3+} – Ti^{3+} pairs (bipolarons) which, at 130 K, undergoes a first Verwey-like transition from a state of bipolaronic order into disorder, without affecting the diamagnetism of the system. The second transition (at 150 K) is explained by a break-off of the bipolarons into paramagnetic polarons of increased mobility [3, 144, 155].

pointed to some further characteristics of the Cullen–Callen model: (i) due to restriction on Coulomb-interactions only—thereby disregarding any type of electron–phonon coupling—self-consistent Hartree calculations are not able to account for any of the experimentally suggested ionic ordering schemes deviating from the Verwey order. (ii) The low-temperature localization may be described as a state of degenerate polarons, permitting charge transport in the form of tunnelling processes, whereas above T_v conductivity is supported by small-polaron hopping—according to the Cullen–Callen model—within a polaron-band. (iii) In order to account for deviations from the Verwey structure, Sokoloff proposes to regard the low-temperature polaron state as a condensate of frozen-in charge-density waves. Another band theory of pair-localized electrons, resembling in some aspects Sokoloff’s view, has been promoted by Buchenau [160, 161]. There is, however, an important difference in the proposed mechanism causing the reduced low-temperature conductivity, which Buchenau explains in terms of Goodenough’s [138] model of electron-pair bonding. Additional arguments for band-conduction have been deduced by Evans [162], upon reviewing and interpreting timely experimental results obtained from resistivity, Mössbauer and heat-capacity measurements.

A most competent band model has been conceived by Ihle and Lorenz [163–166] on the basis of the original Cullen–Callen conception by accounting additionally for both the Anderson condition (section 3.3.2) and the electron–phonon interaction⁹ in the system-Hamiltonian:

$$H = H_I(B, U_1, U_2) + H_{II}(\Phi) \quad (9a)$$

where H_I , similar to the Hamiltonian (8), is composed of two terms accounting for the bandwidth (B)—via nearest-neighbour overlap integrals—and electron correlation (U_1, U_2) expressed here, in view of the Anderson condition, by a two-component effective Coulomb potential: $U = U_1 + U_2$. Correspondingly, U_1 represents the stronger *nearest-neighbour* Coulomb interaction, responsible for the establishment of SRO, whereas the smaller *next-nearest-neighbour* interaction, U_2 , gives rise to the low-temperature (Verwey-type) LRO. These three essential parameters of H_I are assumed to follow the relation¹⁰:

$$U_1 \gg B > U_2. \quad (9b)$$

Sub-Hamiltonian H_{II} of equation (9a) accounts for the interaction with the lattice, as symbolically expressed by the electron–phonon coupling energy Φ . Interestingly, Ihle and Lorenz were able by using only H_I , i.e. in the sole presence of Coulomb SR- and LR-interactions and the absence of any electron–phonon coupling, to exactly reproduce the temperature dependence of the electrical conductivity over the whole range ($65 \text{ K} < T < 500 \text{ K}$) presented in figure 7 [164, 166]. As a necessary condition for the setting-in of

⁹ The existence and influence of electron–phonon interactions has been clearly shown in a study of the oxygen isotope effect on the Verwey temperature [167]. As a result it was found that a replacement of 43% O^{16} by O^{18} led to a shift of T_v by about 6.1 K to *higher* temperatures. This is an indication that due to the large atomic mass of O^{18} the lattice phonon frequency is lowered, thereby stabilizing the ordered phase to higher temperatures.

¹⁰ In order to operate with realistic values for these energy parameters, U_1 , in agreement with the results of various experiments, may be guessed to range within $0.1 \text{ eV} < U_1 < 0.5 \text{ eV}$ so that in the case of electron localization the bandwidth B is expected within the limits $0.03 \text{ eV} < B < 0.17 \text{ eV}$. Two consequences may be immediately deduced from these numbers: (i) the smallness of the bandwidth B —usually of the order of 1–2 eV in transition-metal oxides—is typical for the reduced value of a small-polaron band. (ii) The small value of the effective Coulomb potential, $U_1 \approx e^2/4\pi\epsilon_r\epsilon_0r_{ik}$ (SI), is compatible only with a relatively high value of the relative dielectric constant of about $10 < \epsilon_r < 50$ being feasible only under quasi-stationary conditions [168], thereby supporting—in its turn—the small-polaron view. U_2 may be guessed to be of the order of the thermal energy at the transition temperature, i.e. $U_2 \leq kT_v \approx 0.01 \text{ eV}$.

low-temperature carrier localization and ordering—due to gap formation by band splitting—they deduced the relation

$$U/B > 3 \quad (9c)$$

upon which the conduction process is restricted to small-polaron inter-band hopping. Just above T_v —after gap-shrinkage by about a factor of two, due to formation of sub-bands—the charge transport, up to about 300 K, is mainly supported by band conduction. The observed increase of the conductivity within this temperature range is explained by a corresponding increase of the density of states in addition to a thermally activated destruction of the short-range order [164, 166]. For higher temperatures, $T > 350$ K, the SP conductivity is decreasing owing to a temperature dependent exponential reduction of the polaronic overlapping integral T_{ik} (equation (8)), so that in this temperature range hopping becomes the leading transport mechanism (cf section 4.3.3) in their model.

(3) *Ionic low-temperature ordering models.* As a consequence of numerous experimental and theoretical arguments suggesting a revision of the original Verwey ordering scheme, various alternative topological models have been developed:

- (1) Yamada's model, deduced from neutron scattering studies [55, 56], conceives the freezing-in of Δ_5 -phonon-mode coupled charge-density waves below T_v . This model also laid the basis for the conception of *molecular polarons*, promoted by Yamada to explain the low-temperature electron localization [169].
- (2) Based essentially on NMR, Mössbauer and x-ray results, Iida *et al* devised over the years, depending on the actual state of insight, a series of minutely elaborated ordering models [74, 170–172], of which the most detailed, so-called Mizoguchi model [75] has remained under discussion until today, cf figure 17. Based on this latter, Iida presented an idealized monoclinic, low-temperature superstructure of point group $C_{2h}^5 : P2_1/c$ with two glide planes and eight centres of symmetry in the unit cell [172]. Mizoguchi's model itself, however, though meeting the basic essentials of actually relevant model conceptions ((i) doubling of the unit cell along the c -axis and (ii) observance of the Anderson condition) was found to be incompatible with a specific B -5 hyperfine field reflex in the NMR spectrum and since then is in a state of being 'repaired' by inclusion of various additional effects such as antiphase boundaries and/or twinning [171, 172], cf section 4.4.
- (3) Ihle and Lorenz, by careful analysis of their mathematical model were able to deduce remarkable details concerning charge order in the low-temperature phase [166]:
 - (i) Nearest-neighbour Coulomb interactions U_1 , alone, give rise to SRO formation;
 - (ii) U_1 in combination with next-nearest neighbour Coulomb interactions, U_2 , stabilizes LRO of the Verwey type;
 - (iii) U_1 together with phonon interaction, Φ , (inclusion of sub-Hamiltonian H_{II} (equation (9a)), discarding U_2 , induces Δ_5 -mode, Yamada-type-ordering [56], which is characterized by arrangements of Fe^{2+} – Fe^{3+} ion pairs in a strictly alternating sequence along $\langle 110 \rangle$ (a)-, but in random distribution along $\langle 110 \rangle$ (b)-directions (cf figure 4);
 - (iv) Accounting of U_2 , in combination with Φ , causes additional long-range ordering along the b -axis;
 - (v) In the special case of $\Phi > 2U_2$, so called ab -order is established, giving rise to a modulation of the Δ_5 -mode along the c -axis with wavelength $\lambda = 2a$ —corresponding to a doubling of the unit cell—with unmodulated b -line ordering.

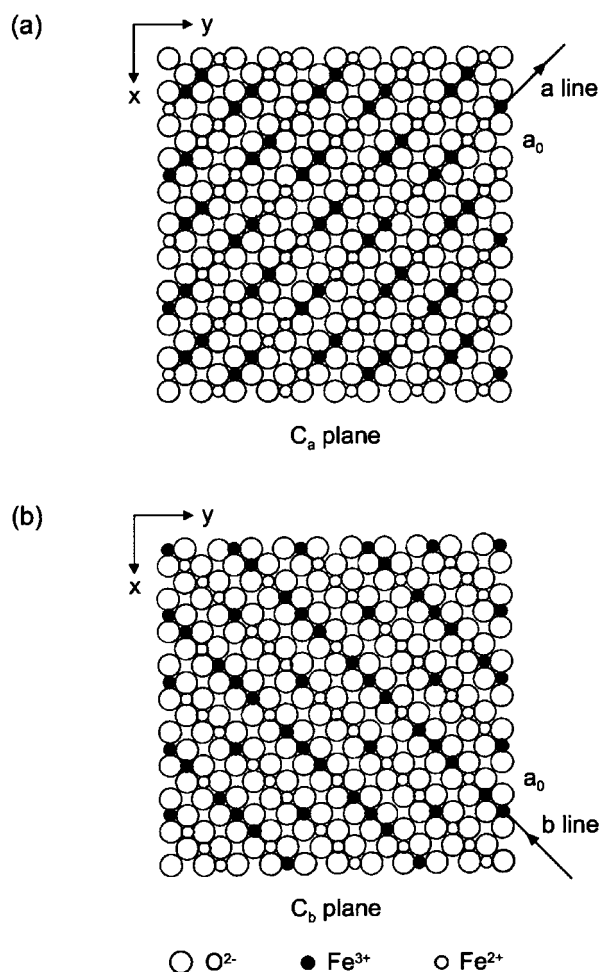


Figure 17. Basic c_a and c_b planes of the Mizoguchi structure which—by alternately stacking along the c -axis in intervals of $a_0/2$, under obedience of the Anderson condition—are constituting the Mizoguchi-type superstructure [75, 171, 245]; cf figure 4, with the lattice parameter $a = 2a_0$.

- (vi) In summarizing their analyses, Ihle and Lorenz were able to design a phase diagram in which the various areas of stable ordering are separated by first-order transition lines [166]. For the extreme case of $\Phi > 10U_2$, two successive transitions are feasible from this diagram.
- (vii) Another deduction drawn from the Ihle–Lorenz model states increased conductivity at temperatures $T > T_v$ due to (a) a spontaneous transition-induced increase of the carrier *concentration* (density of states) at T_v —as opposed to an also feasible increase in their *mobility*—and (b) thermally activated destruction of SRO, assumed to persist above T_v within a certain range $T_v < T < 350$ K, cf section 3.3.2.

Clearly, all these sophisticated ordering models reflect to a certain degree the indefiniteness of the underlying experimental data which frequently have been obtained on imperfect Fe_3O_4 crystals.

4. Verwey transition—progress in era (III) (since 1979)

4.1. Immediate progress after the Mott conference

During the Mott meeting in 1979, two fundamental insights, concerning the experimental side of the magnetite problem, became absolutely clear: (i) the paramount urgency of using only material of the highest perfection in future research, as prepared according to long-known techniques [38–42] which had virtually been applied in masterly fashion by Brabers in the production of perfect single crystalline magnetite [98, 99, 173] and (ii) the advantage of MAE spectroscopy for optimum quality control, due to the high sensitivity of this technique, especially in resolving pronounced spectra in the *low-temperature* phase of Fe_3O_4 where other methods yield only rather unspecific results, cf figure 1, 18, sections 3.2.4, 4.2.3.

4.1.1. Sample quality and control. In agreement with the above, the beginning of era (III) is characterized by a generally growing insight that only by means of carefully prepared high-quality (single) crystals would the unanswered questions on Verwey transition and electron transport in Fe_3O_4 be solved [5, 174, 175]. Honig [5, 175] emphatically recapitulated three essentials of successful crystal preparation: (i) high-purity starting materials, (ii) appropriate growing technique and (iii) homogenization of the crystals. The decisive point during treatments (ii) and (iii) is to accurately control—during *all* phases of preparation—the balance between oxygen partial pressure and temperature according to the well-established phase diagrams [38–42]. Frequently, investigators try to avoid this strict balancing rule during the final cooling phase—from the controlled long-time, high-temperature equilibrium down to room temperature—by rapidly quenching the crystal in a non-adjusted atmosphere. The result of such imprudence is documented in figure 18(d) where a single crystal, prepared by strictest observation of optimum fabrication recipes [5, 175], at the end of high-temperature annealing was rapidly quenched down to room temperature under uncontrolled conditions [176]: by comparison with the perfect Fe_3O_4 spectrum (cf figures 11, 18, 20(b)) we recognize the ‘tunnelling-plateau’ ($4\text{ K} < T < 25\text{ K}$) to be deformed, the hopping plateau ($50\text{ K} < T < 125\text{ K}$) mutilated and, even worse, the apparition of a considerable *B*-site *vacancy-induced* Debye-peak at 300 K.

It is to the credit of Brabers and his group in Eindhoven that, by realizing all preparation conditions—including, especially, the latter one [98, 99]—they were able to produce magnetite single crystals of hitherto *world-wide* unexcelled quality and perfection. This statement is well founded on (i) our rich experience—collected on numerous crystals obtained from colleagues all over the world—by means of (ii) the unique sensitivity of our MAE technique to the lowest-temperature processes in magnetite (cf figures 11, 18, 20(b)), which react with utmost sensitivity on any deviation from the perfect crystal state—induced by impurities, defects or structural deficiencies. Moreover, the MAE spectrum obtained on Brabers’ Fe_3O_4 single crystals—characterized by [SSC, 125 K] and abbreviated henceforth by BRA—corresponded exactly to the extrapolations we were able to deduce from our own, less perfect, polycrystalline samples (cf figure 11).

4.1.2. Elimination of multi-stage ($n > 2$) transition models. The discussion and comparison of experimental results under the aforementioned aspects—revealing the bad sample quality on which the multi-stage interpretations were founded (cf figure 18(b))—led, as an immediate consequence of the 1979 conference, to a complete withdrawal of multiple transition models in connection with perfect Fe_3O_4 (cf section 3.2.2). Indeed, no further serious attempt has

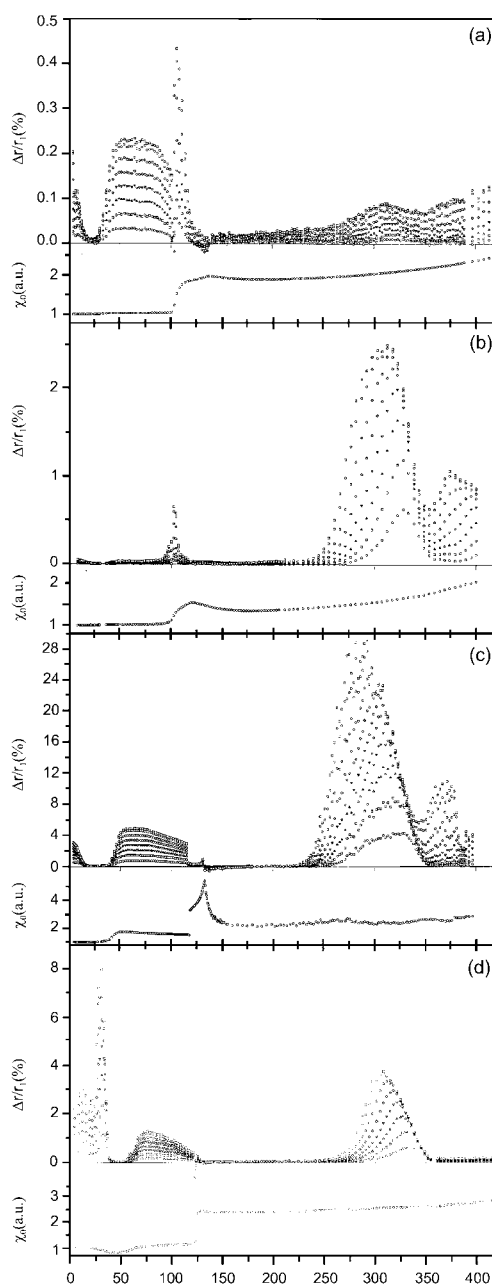


Figure 18. Demonstration of MAE spectroscopy as a highly sensitive probe of crystal quality: (a) natural magnetite single crystal (Saas Fee, Egginer Joch, Switzerland); (b) polycrystalline magnetite, prepared by oxidizing a high-purity Fe rod as described in [86]. Based on results obtained from material of such (poor) quality, multi-stage transition ($n \leq 12$) has been proposed, cf [85–88, 92]; (c) synthetic single crystal, as obtained from Chikazumi in the midst of the 1970s [185], revealing serious deficiencies; (d) synthetic single crystal—as prepared by state of the art methods [38–42], including Honig’s recipes [5, 175]—but, unfortunately, quenched at the end of the thermal treatment, thereby considerably spoiling the quality by introduction of stress (deformation of the two plateau relaxations associated, respectively, with incoherent tunnelling and hopping) and B-site vacancies (appearance of the 300 K peak) [176].

been undertaken, since then, to associate the Verwey transition of unperturbed magnetite with multi-stage processes [177, 178].

4.1.3. Elimination of bifurcation in specific heat. Despite Matsui *et al*'s [82] clear results concerning this problem, cf section 3.2.2, the relevance of a second peak near 110 K, besides the major one at T_v , remained under discussion for many further years. Whereas Rigo *et al* [84, 179, 180] regarded this second peak—obtained on powdered material—as purely intrinsic, Gmelin *et al* [181, 182] and Shepherd *et al* [183], on well prepared single crystals, could not detect any trace of this 110 K anomaly. The final ‘knockout’ for the thermal bifurcation, as an intrinsic process of *perfect* magnetite, was accomplished by means of the MAE [184]. We had the chance to compare the spectra of two samples of originally the same BRA-type basis material: (i) an unaltered, as-perfect bulk single crystal and (ii) the modified version of such a BRA-crystal, as obtained by Rigo after a powdering and subsequent annealing. Our MAE analysis revealed significant deviations between the spectra of the powdered and perfect crystals which could be unambiguously associated with the presence of internal stresses and *B*-type vacancies which had been introduced during the powdering process [184]. On the occasion of this test we were also able to finally exclude, as had already been done previously [185], the occurrence of a further, long-debated anomaly at 10 K [172, 179–183], which initially had been reported by Todo *et al* [186]. These final MAE results have been confirmed by further specific heat investigations performed since then [187, 188]. Thus, a first important result obtained in the ‘post-Cambridge’ era (III), by means of specific heat and MAE analysis, consists of the definitive statement that in perfect magnetite, within the temperature range $4 \text{ K} < T < 500 \text{ K}$, there exists only one *unique* Verwey transition occurring near 125 K as a first-order process. Accordingly, most of the abundant number of papers—mentioned in [5]—reporting over many decades on exotically complicated (multi-stage) phase transitions in magnetite were *wrong—insofar* as they regarded their observed effects as being typical for *perfect magnetite*—instead of associating them with the deficiencies of their actually *imperfect sample material* concerning stoichiometry, purity, stress-release etc.

4.2. Further experimental progress in era (III) (since 1979)

4.2.1. Crystallographic structure. Investigation of crystallographic structure has remained a subject of continued efforts by means of various techniques. Iizumi *et al*, using neutron diffraction [189], confirmed the previously determined C_c symmetry for the low-temperature phase ($T < T_v$) of Fe_3O_4 (cf section 3.2.1), characterized by a four-fold increased monoclinic unit cell, of $\sqrt{2}a \cdot \sqrt{2}a \cdot 2a$, as compared to the cubic, O_h^7 : $F3dm$ -structured high-temperature ($T > T_v$) phase. The same result was obtained by means of high-resolution electron microscopy (HREM) [190, 191], with Otsuka *et al* [190] estimating the small deviations from C_c symmetry, as predicted from magneto-electric studies [76–78], to lie outside the detection limit of HREM. Renewed magneto-electric studies, performed by Myamoto *et al* [192], revealed, as a function of applied stress, up to six different twinning modes pointing to a crystal symmetry of triclinic-1 type below T_v . From a recent analysis of NMR results, Mizoguchi [193] also deduced deviations from the former C_c crystal symmetry: the observed splitting of the NMR spectra, revealing the existence of eight non-equivalent A-site positions—one of which displaying mirror symmetry with respect to the *ac*-plane—is incompatible with the hitherto assumed C_c symmetry and thus indicates further modified crystallographic order.

4.2.2. Electric charge transport.

(1) *Low-temperature conductivity* ($T < T_v$) and magnetic after-effects in Fe_3O_4 have been identified as two aspects of the same mechanisms controlling ionic valence exchanges according to equation (1) by thoroughly investigating, using both techniques, the temperature dependence of single crystals of different quality, characterized by the spectra of figures 18(c) and 11(c) [194]. As reported previously by Drabble *et al* [95], the conductivity is found to be thermally activated in the temperature range from below T_v to about 50 K, thereby following a $T^{1/4}$ temperature dependence as derived by Mott [3] for the case of variable range hopping (VRH). Interestingly, this temperature interval ($50 < T < 125$ K) coincides with the occurrence of an extended plateau-like MAE spectrum (cf figures 11(c), 18(c)) which, independently, has been associated with small-polaron hopping [121, 123–125, 195]. In true agreement with the occurrence of *two* different MAE processes in the low-temperature range of the perfect crystal—i.e. a further plateau-like spectrum ($4 \text{ K} < T < 25 \text{ K}$), culminating in a Debye peak (30 K) with ensuing MAE gap (up to $T < 50$ K)—*two* additional intervals with different conductivity activation are observed within $4 \text{ K} < T < 25 \text{ K}$ and $25 \text{ K} < T < 50 \text{ K}$, respectively [194]. Similar agreement is observed for the less perfect crystal where only *one* (damaged) plateau-like MAE ($4 \text{ K} < T < 25 \text{ K}$), again followed by a gap (up to $T \approx 35$ K) corresponds to only *one* further conductivity interval extending between $4 \text{ K} < T < 35 \text{ K}$. Following the analyses by both techniques, these low-temperature processes have been identified as thermally activated, incoherent electron tunnelling ($4 \text{ K} < T < 25 \text{ K}$) and intra-ionic electronic excitation.

A similar $T^{1/4}$ dependence of the conductivity, extending in the temperature range $T_v > T > 30$ K, has been observed by Kobayashi *et al* [196], where the low-temperature range ($T < 30$ K) was found to deviate from this relation. On studying the influence of pressure on the Verwey transition (T_v) and on low-temperature conductivity of Fe_3O_4 , Rozenberg *et al* [197] also observed—in qualitative agreement with preceding investigations [103, 104], cf figure 19—for temperatures $T_v > T > 30$ K and pressure below 16 GPa, the VRH-specific $T^{1/4}$ law, failing again for temperatures $T < 30$ K. On recent resumption of Rozenberg *et al*'s investigations, Todo *et al* [198] yielded modified results: with increasing pressure, P , they find nonlinear, instead of the former linear, decrease of T_v up to pressures of $P \leq 8$ GPa, above which the transition is completely suppressed. Below T_v , in the range $7.5 < P < 8$ GPa, the conductivity dependence on temperature is of 'metallic' type—i.e. $\sigma(T)$ decreasing with T , instead of increasing as expected for electron hopping and actually observed in stress-released Fe_3O_4 (cf figure 7). In the transition-suppressed range, $P \geq 8$ GPa, this type of conduction—in contrast to former observations below [103, 104, 197] and above this limit [197]—dominates the whole temperature range ($3 \text{ K} < T < 300 \text{ K}$). These discrepancies, relative to the former results are associated, by [198], with imperfectly realized hydrostatic conditions in the earlier experiments—to what extent different sample quality may have contributed to these divergencies remains an unsettled question in view of the insufficient crystal characterization of these investigations. *Thermopower measurements* have been resumed which, though providing new insights concerning location and acuity of the Verwey transition as a function of B-site vacancies ($\text{Fe}_{3(1-\delta)}\text{O}_4$: $0.0005 < \delta < 0.012$) [199] and applied pressure ($0 < P < 6$ GPa) [200], could not completely reproduce the detailed information obtained previously by Kuipers *et al* [98, 99] on quasi-perfect BRA-type Fe_3O_4 single crystals. Thus, possibly due to reduced measuring range and/or minor sample quality, no low-temperature sign change of the thermopower, as in [98, 99] has been observed (cf section 3.2.4) in recent studies [175].

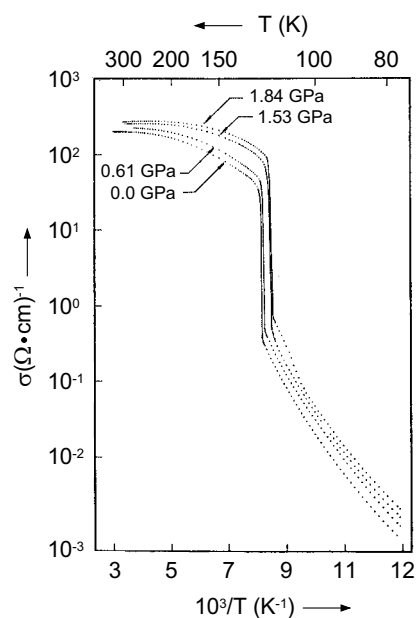


Figure 19. Influence of pressure on the temperature dependence of the electric conductivity and the Verwey transition in Fe_3O_4 [104].

(2) *High-temperature conductivity* ($T > T_v$) has been recently studied by means of various techniques, yielding results which have been differently interpreted by their authors in terms of either polaron hopping or band conduction. Todo *et al* [201], from conductivity and Hall effect measurements [SSC, ~ 123 K], deduced charge transport of possibly large-type polarons within the range $T_v < T < 250$ K, with rather small stoichiometry dependence ($\text{Fe}_3\text{O}_{4+x}$) within the range $0.002 \leq x \leq 0.035$). Similarly, Nakamura *et al* [202] interpreted their Mössbauer spectra, obtained at temperatures ≤ 300 K on crystals of comparable quality, in terms of large polaron conduction. Boekema *et al* [203] concluded from their muon-spin-relaxation data, for $T > T_v$, that the carriers formed a Wigner-glass phase, supporting conduction in the form of phonon-assisted electron hopping within a narrow polaron band as suggested by Mott [3]. In terms of similar arguments, Siratori *et al* [204] and Degiorgi *et al* [205] described their data obtained from, respectively, neutron diffuse scattering [SSC, 122.5 K] and optical- combined with dc-conductivity [NSC, ~ 120 K] studies. As in preceding works (cf section 4.3.2), the optical results were deduced from low-energetic spectra ($0.001 \text{ eV} < E < 0.6 \text{ eV}$) and analysed in terms of the Ihle-Lorenz model [148, 170], combining the small-polaron (SP) concept with Anderson's short-range order. On this basis, dc-conductivity within $100 \text{ K} < T < 450 \text{ K}$ can be well described by a superposition of SP band and hopping conductivity [148]. The old problem, concerning the Verwey transition being of metal-insulator¹¹ or rather semiconductor-insulator type, stood, once more, in the focus of recent photo-emission studies. Chainani *et al* [206, 207] deduced a metal-semiconductor transition from their observation [SSC, 122 K] of a gap of 0.07 eV, separating the low- and high-temperature phase, which closes upon heating above T_v . Park *et al* [208, 209] countered with further experiments [SSC, 121 K], pointing to a semiconductor-insulator transition at T_v . They, too, found a gap (of about 0.14 eV) between the

¹¹ A more correct notation would be 'semiconductor-semiconductor transition between two states of different conductivity' (differing by a factor of about 100).

two phases which, however, instead of becoming closed above T_v was only narrowed by about 0.05 eV. Consequently they associated this narrowing with the loss of long-range order above T_v giving rise to the observed conductivity jump. Gasparov *et al* [210] found their infrared and Raman data [SSC, 120 K] best explained in terms of polaronic pictures. Below T_v they deduced strong polaron localization, as expressed by an approximately hundred-fold increased effective mass indicating the role of lattice dynamics. The increased conductivity above T_v is explained by partial delocalization of carriers in agreement with Park *et al*'s conceptions.

4.2.3. *MAE contributions to model designing.* For our Stuttgart MAE group, probably the most decisive event—at the eventful 1979 Mott conference in Cambridge—was the chance to become personally acquainted with Victor Brabers and to gain his trust in our MAE technique to the extent that he offered us one of his perfectly synthesized magnetite single crystals. In our search to find the ideal MAE spectrum of magnetite—i.e. the spectrum corresponding to perfect magnetite—the results obtained on this crystal provided the keystone of our preceding endeavours [120–125] and allowed us to interpret the observed effects, according to figures 11(c), 20(b) as follows [185, 195, 211].

The spectrum of ideal magnetite is composed of three parts: (1) a low-temperature plateau, already activated below $T = 4.2$ K and culminating into a pronounced, Debye-type relaxation peak near 30 K; (2) a second, similar plateau-like relaxation extending between $50 \text{ K} < T \leq T_v (\simeq 125 \text{ K})$, being separated from the former one by (3) a distinct relaxation-free gap located between $35 \text{ K} < T < 50 \text{ K}$. Of these processes, the two plateaus have been associated with different mechanisms of electron transfer, i.e. (1a) interatomic, *incoherent* e^- -tunnelling ($T < 25$ K, section 4.4.2), (1b) intra-atomic e^- -excitation within the crystal-field split level system (30 K); (2) thermally activated small-polaron hopping ($50 \text{ K} < T < 125 \text{ K}$) [194, 195, 211]; (3) the gap between the two relaxation plateaus marks a temperature span within which thermal activation, on the one hand, is intense enough to equilibrate the low-temperature processes prior to our minimum observation time ($t < 1$ s) but, on the other hand, still too weak to initiate the second, higher-temperature plateau process.

The basic items of the MAE spectroscopy may be summarized as follows:

- (i) The MAE as a highly-sensitive, systematically time-resolving technique has the advantage of dynamically following and distinguishing between the various motion modes of carriers below T_v .
- (ii) The appearance of characteristic MAE spectra only in the low-temperature ($T < T_v$), as opposed to the high-temperature ($T > T_v$) range, is a clear indication of electron localization, causing a drastic reduction of the interionic exchange frequency below T_v (equation (1)).
- (iii) Different mechanisms of electron exchange can be clearly distinguished in the MAE spectrum, being associated with thermally activated small-polaron hopping ($50 \text{ K} < T < T_v$ (125 K)) and incoherent tunnelling ($T < 30$ K).
- (iv) Whereas from the MAE spectra, *per se*, no direct information on any type of *specific* ionic ordering scheme is deducible, the existence of *ionic ordering*, in general—superimposed on electron *localization*—is clearly indicated by the dramatic jump at T_v and further continued decrease of the initial susceptibility, attaining a minimum near $T \simeq 30$ K, cf figures 11(c), 20(b).

Such ionic ordering is also suggested by the high sensitivity of the two plateau-type relaxations on smallest deviations from the perfect crystal state, cf figure 18. Whereas the occurrence of the low-temperature *tunnel plateau* ($4 \text{ K} < T < 25 \text{ K}$), *per se*, is bound to a high degree of ionic ordering, the *hopping plateau* points to such ordering by its perturbation-dependent temperature

extension ($50 \text{ K} < T < 125 \text{ K}$) and relaxation strength. These two parameters react on loss of order by, respectively, restriction of variable-range-hopping and reduced hopping-induced lattice polarization [125], thus giving rise to *narrowed* plateaus with *increased* amplitudes, cf figures 18(c), (d) and 20(b).

The high sensitivity of the *low-temperature* MAE spectra on minute deviations from the perfect crystal state permitted us to contribute to a clarification of various magnetite problems, like multi-stage ($n > 2$) transitions (section 4.1.2) and thermocaloric bifurcation (section 4.1.3).

In order to further develop our MAE-based conceptions of charge transport and relaxation in Fe_3O_4 , we investigated a series of single crystals and polycrystals with systematically perturbed stoichiometry. Intrinsic lattice defects were introduced by means of low-temperature electron (e^-) irradiation [195], yielding B- and A-type vacancies and interstitials which upon subsequent annealing are observed to mainly recombine directly with their respective antidefects and to coalesce, in minor number, into small clusters. An interesting aspect of these investigations is the occurrence of pronounced interstitial-induced internal stresses, giving rise to anomalous spike-like relaxations near 120 K. On annealing up to $T_a \leq 500 \text{ K}$ all irradiation-induced lattice defects have again been completely annihilated.

Complementarily, the reaction of the MAE spectra of polycrystalline Fe_3O_4 on systematically doping with (i) B-site vacancies ($\text{Fe}_{3-\delta}\text{O}_4$) [120–124] or impurity ions ($\text{Fe}_{3-x}\text{M}_x\text{O}_4$) like $\text{M} = \text{Mn}^{2+}$ [122, 212], Ba^{2+} [213], Ni^{2+} [214], Zn^{2+} [215, 216], Ti^{4+} [217, 218], Ga^{3+} [219] has been investigated. The basic effects of these treatments may be summarized as follows (section 3.2.4(3)):

- (i) The low-temperature tunnel-plateau with adjoint Debye peak ($4 \text{ K} < T < 35 \text{ K}$) reacts most sensitively on imperfect stoichiometry and for defects contents $x, 3\delta > 0.01$ is practically completely suppressed (cf [175]).
- (ii) At these defect contents, the hopping-plateau ($50 \text{ K} < T < 125 \text{ K}$), though still present, is considerably reduced in temperature extension and amplified in strength.
- (iii) The high-temperature decay of this plateau, intimately associated with the transition at T_v , becomes flattened and shifted to lower temperatures ($T_v < 110 \text{ K}$), whereas the transition itself changes from first to second order, before completely disappearing (at $T_v \simeq 100 \text{ K}$) cf [184].
- (iv) The defect-induced relaxations above T_v , i.e. 300 K peak (B-site vacancies) and higher-temperature satellites (B-site impurity substitutes), are found to monotonously grow with respective defect concentrations.

It seems relevant to report here a most interesting observation made recently on low-temperature ($T \leq 80 \text{ K}$) e^- -irradiated single crystalline yttrium iron garnet (YIG). In the course of a systematic, extremely extended annealing programme ($80 \text{ K} < T_a < 1400 \text{ K}$!), there appeared at an intermediate annealing stage ($T_a = 573 \text{ K}$) a low-temperature MAE spectrum¹² of striking similarity with the well-known spectrum of perfect Fe_3O_4 (cf figures 20(a), (b)) [221]. This surprising effect is explained by an irradiation-induced perturbation of the initial charge equilibrium due to a transformation of a larger number of Fe^{3+} into Fe^{2+} ions (within the related perovskite lattice), able to interact with one another, according to equation (1), quite similarly as in the low-temperature phase of Fe_3O_4 —after annihilation of some initial, disturbing defect configurations during annealing up to a first

¹² Usually, YIG is regarded as an insulator and one would not expect any MAEs, based on equation (1), at all; actually, however, we observe already in our unirradiated single crystals—due to small deviations from perfect stoichiometry—a minor rather unstructured MAE spectrum within the range $4 \text{ K} < T < 350 \text{ K}$ [220, 221]. After e^- -irradiation, this initial spectrum is characteristically modified and dominated by the interactions of the irradiation-induced defects.

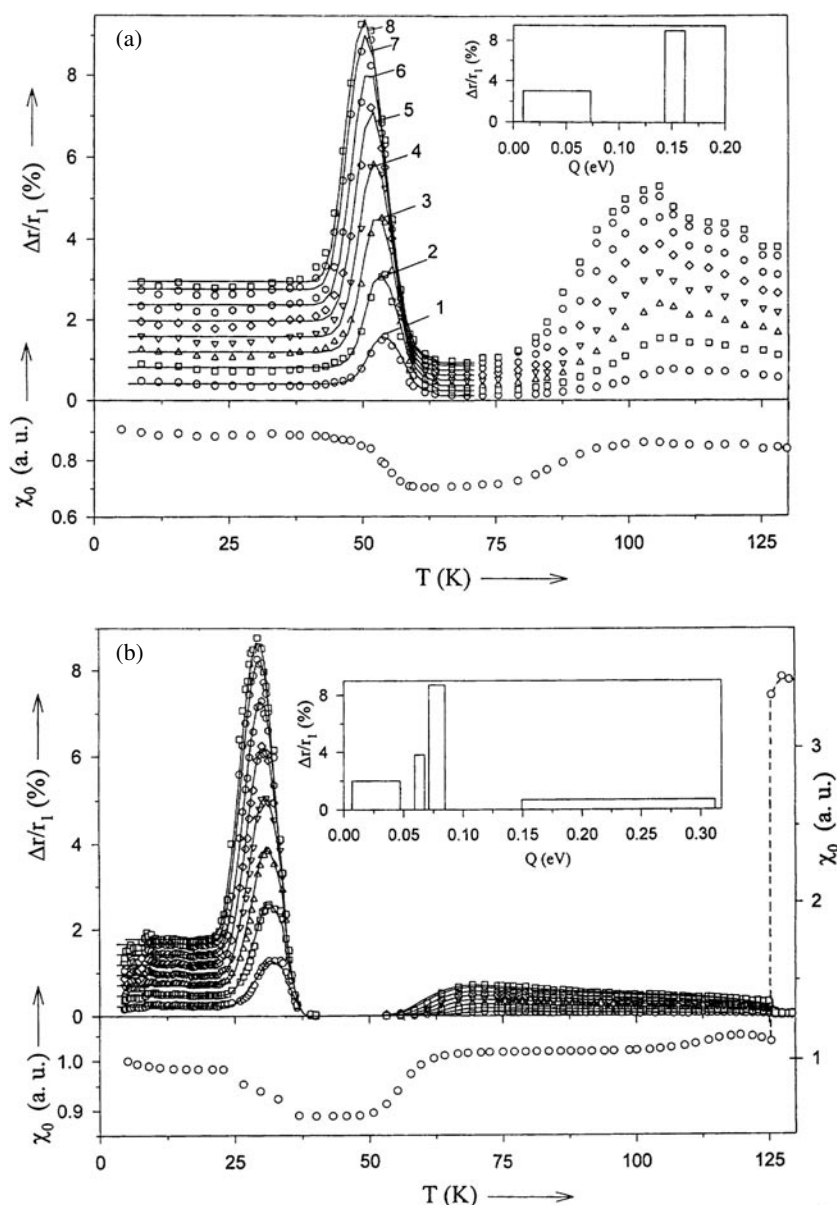


Figure 20. (a) Low-temperature spectrum of e^- -irradiated YIG after intermediate annealing to $T = 573$ K, together with the initial susceptibility, χ_0 [221]; (b) related low-temperature spectrum of perfect (BRA-type) single-crystalline magnetite, presented correspondingly to (a) [185]. In both figures (a) and (b) the isochronal relaxation families are depicted as described in figure 11. The insets show the energy distributions of participating processes—as determined from numerical fitting (continuous curves) of the experimental data (symbols).

stage of $T_a = 573$ K. Insofar as this interpretation is regarded as correct, the interrelated YIG spectrum tells us that a prerequisite to incoherent low-temperature tunnelling is short-range order—which may be assumed to have been established also in e^- -irradiated YIG—in contrast to LRO which can be excluded in view of the absence of any observable transitions

within the range $4 \text{ K} < T < 500 \text{ K}$. This situation is in agreement with Mott's view of a low-temperature Wigner crystallization permitting small-polaron tunnelling within narrow bands. Upon intensified phonon interaction with increasing temperature these bands become destroyed (at temperatures $\gtrsim 50 \text{ K}$), thereby confining charge transport on variable-range hopping of small polarons. Whereas in YIG this mechanism is steadily continued over the whole temperature range ($50 \text{ K} < T < 350 \text{ K}$) [220–223], it becomes drastically modified in Fe_3O_4 upon passing the Verwey transition, as described in the foregoing.

4.3. Progress in theoretical model designing (since 1979)

Starting from their fundamental presentation in 1980 [166], Ihle and Lorenz further refined their model in the following years and confronted it directly with experimental results. By comparison with pressure experiments they were able to quantitatively describe the shift of T_v as a function of pressure and to determine representative values for the parameters entering into their model, cf section 3.3.3, i.e. $U_1 \leq 0.5 \text{ eV}$, $U_2 \approx 0.3kT_v = 0.003 \text{ eV}$, $B \approx 0.08 \text{ eV}$ [224]. In repeated attempts they assessed—with remarkable success—the problem of high-temperature electric [148, 225, 226] and optical [205] conductivity in terms of their spinless small-polaron model [166]. Direct band structure calculations for the high-temperature magnetite phase have been performed by Yanase *et al* [227], using augmented plane wave (APW) approximations. Concerning the band structures of B-sited Fe ions they found the Fermi level, E_F , to lie within the minority t_{2g} bands (width $\sim 1 \text{ eV}$), in contrast to the majority bands where E_F crosses a gap. Under this aspect the authors suggested discussing the conductivity problem in Fe_3O_4 in terms of itinerant rather than localized electrons.

Another band calculation approach has been made by Zhang *et al* [228] using local spin density approximations (LSDA) in combination with density functional techniques. On account of the xy -, yz - and zx - t_{2g} orbitals of the minority state electrons they used an extended triplet-band Hamiltonian of the Cullen–Callen type (cf section 3.3.3)

$$H = \sum_{i,k} \sum_{\mu,\nu=1}^3 T_{\mu\nu} c_{i\mu}^{\dagger} c_{kv} + \sum_{i,k} \sum_{\mu,\nu=1}^3 U_{i\mu,k\nu} n_{i\mu} n_{kv}. \quad (10)$$

The indices (i, k) and (μ, ν) denote, respectively, the three orbitals and positions of the B sublattice; $T_{\mu\nu}$ represents the hopping and $U_{i\mu,k\nu}$ the Coulomb interaction term. Spinless presentation of this Hamiltonian is used here since, as in the preceding work [227], only minority-type extra-electrons are found to exist at the Fermi level. Corresponding to the treatment of Ihle and Lorenz (cf section 3.3.3), the Hamiltonian (9) is characterized by the bandwidth B ($T = T(B)$) and the Coulomb potential $U = U(U_1, U_2)$, with U_1 and U_2 denoting nearest and next-nearest neighbour interactions. The determined parameter values— $B = |0.13| \text{ eV}$, $U_1 = 0.3\text{--}0.4 \text{ eV}$ and $U_2 \approx 0.05\text{--}0.1 \text{ eV}$ —are in agreement with the Cullen–Callen–Ihle–Lorenz (CCIL) criterion $U_1/B \geq 3$, thus suggesting to describe the low-temperature localization (due to band splitting) and Verwey-type ordering of carriers in terms of a purely electronic Hamiltonian, i.e. by discarding the contributions due to B and U_2 . Inclusion of B transforms the Verwey order into a lower-symmetric pattern which, on accounting also for U_2 , undergoes long-range ordering, i.e. of (modified) Mizoguchi type [229]. Band structure calculations of similar relevance have been performed by Pénicaud *et al* [230], who included into their considerations, besides Fe_3O_4 , also Co-, Ni-, Mn- and Zn- ferrites.

Anisimov *et al* [231, 232] resumed the foregoing LSDA band structure calculations which, as immediate solutions, had provided gap-free, metallic band-structures, without any chance for charge ordering, in contrast to the photo-emission results which indicated gaps of about $\Delta E \approx 0.15 \text{ eV}$ [206–209]. They explained this discrepancy by arguing that ordinary LSDA

inherently contains some spurious contributions of self-interaction which are responsible for the hitherto obtained, unrealistic results. In order to compensate for this obvious handicap, they introduced an extra Coulomb interaction potential U , thus arriving at the so-called $LDA + U$ method [232], by means of which they were able to reproduce realistic band structures with gaps of the order $\Delta E \approx 0.34$ eV, in qualitative agreement with experiments.

In a pragmatic attempt, the group around Honig [175, 233, 234] developed a phenomenological description of the Verwey transition in terms of the two-state molecular-field approximation designed by Strässler and Kittel [235]. The decisive parameters entering into this model—i.e. ε , the gap energy between the two states; λ , an effective interaction term; g_0 and g_1 , the degeneracies of the two states—are numerically determined, from fittings to the experimental data. This strategy enabled Honig *et al* to adequately describe the shift of the critical temperature, T_v , including the conversion of the transition from first to second order as a function of systematically increased non-stoichiometry by doping with B-site vacancies ($\text{Fe}_{3(1-\delta)}\text{O}_4$) or substitutional impurities ($\text{Fe}_{3-x}\text{M}_x\text{O}_4$) [175, 234], M denoting e.g. Zn^{2+} or Ti^{4+} [236]. After extension of this mean-field theory by an attempt phonon frequency, ν_0 (assuming different values $\nu_0 \approx 10^{10} \text{ s}^{-1}$ and $\nu_0 \approx 10^{-13} \text{ s}^{-1}$ below and above T_v , respectively), the electrical conductivity is approachable over the range $77 \text{ K} < T < 500 \text{ K}$ in terms of small-polaron hopping.

As compared with a clearly composed ‘first principle theory’, of the Ihle–Lorenz type [166], discriminating and accurately accounting for the various effective interactions, some shortcomings of the pragmatic design by the Honig group are obvious: (i) since, implicitly, only next-nearest neighbour Coulomb interactions are considered, no information on low-temperature charge ordering is deducible. (ii) The Anderson condition being discarded in this treatment, the respective Verwey transition is found to be accompanied by the ‘wrong’ entropy change of $S_v = R \cdot \ln 2$ [147, 148] (corresponding to a full-order/complete-disorder transformation) instead of only half this value as expected in the case of an Anderson LRO–SRO disordering, as has been actually determined in experiments (cf section 3.3.2(5)). (iii) Typical for this type of phenomenological theory, no experiment-independent quantitative prognostics of basic process parameters, i.e. the correct value of the transition temperature, T_v , are feasible.

Being aware of these handicaps, Brabers *et al* [237–239] experienced as to what extent an alternative two-state mean-field model, accounting only for Coulomb SR- and LR interactions—which, according to previous analyses [166] should dominate the low-temperature phase—may be successful for a quantitative description of the Verwey transition and associated parameters of Fe_3O_4 in the temperature range around T_v . Thus, in terms of the Ihle–Lorenz formalism, cf equations (8), (9) [166], only the Coulomb interactions U_1 and U_2 —as determined from a Madelung approximation over nearest and more distant neighbours—have been accounted for, whereas kinetic (T_{ik}) and phononic (Φ) contributions were neglected. This strategy yielded, quite straightforwardly, a series of quantitative predictions which are in satisfactory agreement with respective experimental results:

(a) *The transition temperature* was found to follow the relation

$$T_v = W/8k \quad (11)$$

where the energy gap, W , separating the two electronic sub-bands of the assumed two-state model, is estimated from thermopower [98, 240] and photo-emission data [208] to be about $W \approx 0.1$ eV, thus resulting in $T_v \approx 145$ K as compared to the experimental value of $T_v \approx 125$ K [237].

(b) When approaching from low temperatures, this gap gradually closes due to thermally induced disorder, thereby giving rise to increased inter-band hopping conductivity. Thus,

the disappearance of the gap at T_v marks—formally—a semiconductor–‘metal’ transition with, however, the conductivity in the high-temperature range suggested to result from small-polaron intra-band hopping. The problem as to whether the transition in a given system is governed by first or second order, has been found to depend intimately on volume-sensitive LR Coulomb interactions, as evoked by transition-induced lattice distortions [238].

- (c) In quantifying these considerations, the following relations were deduced concerning the pressure dependence of T_v [238]:

$$\frac{dT_v}{dp} = -\frac{6}{7} \frac{\Theta}{N \cdot k} \quad (12)$$

with Θ , N , and k denoting, respectively, the relative volume variation ($\Delta V/V = 6 \times 10^{-4}$ at T_v for $p = p_0$ [62]), the number of Fe^{2+} -type extra electrons per m^3 ($N = 8 \times [8.39 \times 10^{-10}]^{-3} = 1.35 \times 10^{28} \text{ m}^{-3}$) and the Boltzmann constant. Since a linear dependence between T_v and hydrostatic pressures up to 6 GPa has been experimentally established [103, 104, 197, 241], the value determined from relation (11) to $dT_v/dp \simeq -2.76 \text{ K GPa}^{-1}$ is representative for this whole linearity range and, indeed, in fair agreement with the literature data, varying between $-2.0 < dT_v/dp < -5.0 \text{ K GPa}^{-1}$ [103, 104, 197, 241].

- (d) Another feature of this model is the correct description of T_v shifting as a function of systematic substitutional impurity (x)- or B-site vacancy (δ)-doping within the (relatively small) concentration range $0 \leq x, 3\delta < x_c, 3\delta_c$ —with $x_c, 3\delta_c \simeq 0.013$ [175, 187, 242]—corresponding to the first-order regime, beyond which the transition is governed by second order. The various dopants may be distinguished into two groups as to whether upon their introduction the ratio M^{2+}/M^{3+} of B-site ions is either (i) unchanged or (ii) varied. In both groups T_v shifting, relative to $T_{v,0}$ in perfect Fe_3O_4 , follows a linear relation of the type:

$$\Delta T_v = -\alpha_{i,ii} \cdot y T_{v,0} \quad (13)$$

where $\alpha_i \simeq 3$ for group (i) metallic B-site substitutes ($y \hat{=} x$)—like Ni^{2+} , CO^{2+} , Mg^{2+} and Ga^{3+} —also including B-site vacancies ($y = 3\delta$) [242, 243] and $\alpha_{ii} = 9(y \hat{=} x)$ in the case of group (ii) metallic solutes, i.e. Zn^{2+} (A) and Ti^{4+} (B), importing ‘wrong’ valencies into the respective sublattices. Interestingly, group (i) elements invariably follow relation (12) up to the concentration limit, $x_L \leq 3x_c$ (0.039), beyond which the so-long surviving second-order transition becomes finally suppressed, whereas the corresponding group (ii) relation is characterized by a reduced inclination, α_{ii}^* , within the high-content interval $x_c < x < x_L$ [175, 243, 244].

- (e) Phase stability considerations yielded a Cullen–Callen-type criterion stating LR low-temperature ordering to become effective only for strong enough Coulomb interactions, expressed by an interaction parameter β , in relation to the band-width W , i.e. for ratios $\beta/W \geq 1$ [239].
- (f) The temperature dependence of the conductivity on both sides of T_v , e.g. within a range of about ($50 \text{ K} < T < 300 \text{ K}$), is described according to Mott [3], in terms of (i) low-temperature *Wigner-crystallization* (carrier localization) caused by band-splitting due to electron-correlation and/or electron–phonon interactions, restricting charge transport on thermally activated inter-band hopping and (ii) enhanced high-temperature small-polaron hopping within narrow bands, having formed upon $T \geq T_v$, under obedience of the Anderson SRO condition, thus constituting a *Wigner-glass*.

The efficiency of this elementary model in producing quantitative solutions of correct order of magnitude for a series of problems is not only a success in itself but also a confirmation of Ihle

and Lorenz's well-structured theoretical treatment [166], in which the Coulomb SR and LR interactions are regarded as the basis for first-order approaches to the Verwey transition and conductivity mechanisms in magnetite—although Ihle and Lorenz, on the other hand, prefer a somewhat modified band-type description (cf sections 3.3.3, 4.2.2).

Clearly, in order to obtain higher-order accuracy—concerning quantitative results of system parameters, conductivity and ionic ordering—all relevant interactions are to be cared for, as recently pointed out with regard to the kinetic electron energy (hopping-integral T_{ik}), mainly under theoretical band structure aspects, by Mishra *et al* [245] and with respect to electron–phonon interactions, from an experimental point of view, by Kakol *et al* [246], cf section 3.3.3. The successful Coulomb approach of Brabers *et al* [237–239], however, supports the relative role assigned to the various interactions, in terms of the Ihle–Lorenz conception [166].

4.4. Progress in ionic ordering schemes

(1) *Mizoguchi-type low-temperature ordering.* After the break-down of the original Verwey ordering model under the burden of experimental proof, cf section 3.2.1, out of the alternatively proposed ordering designs the Mizoguchi model (MM) proved to be the most promising, despite its early-discovered incompatibility with the appearance of the so-called B-5 hyperfine-field reflex in the NMR spectrum, cf section 3.3.3. The primary handicap of the original MM, as compared with the Verwey model, of having the higher Coulomb energy, has been resolved by Mishra *et al* [245] by taking into account additional terms of the complete system Hamiltonian [166] when minimizing the overall energy. Thus, they found that for Coulomb energies up to $U_1 \leq 0.25$ eV, the inclusion of the kinetic electron energy (T_{ik}) already leads to a sufficient energy reduction, whereas for U_1 above this limit, phonon interactions have to be considered additionally. In terms of this view, Wiesendanger *et al* explained their scanning tunnel microscopy results, in which they were able to resolve a MM-type ionic ordering on a carefully prepared magnetite surface [NSC, 98 K (!)] [247]. They assumed the energetic contributions to be of such an order as to establish in the bulk, below T_v , MM-type ionic ordering according to the localization conditions $U/B > 3$ [166]. Whereas, however, above T_v in the bulk this order is destroyed, they postulate it to be frozen-in on the surface up to room temperature (!) due to extreme perturbation-induced band-narrowing.

Continued attempts to overcome the structural incompatibilities of the MM with most other experimental observations have been undertaken by tentatively introducing additional symmetry elements like antiphase boundaries and twinning [172, 248–250]. Detailed analyses have been performed concerning the availability of alternative ordering schemes which, however, had to obey the unabandonable low-temperature essentials: (i) doubling of the unit cell along the c -axis (monoclinic C_C symmetry) and (ii) compliance with the Anderson condition. Under these constraints, Kita *et al* [251] and later Zuo *et al* [191] separated ten feasible models. Especially the latter investigations revealed, once more, the distinction of the Verwey model with respect to a minimum electron correlation energy. This model being outdated, however, Zuo *et al* proposed as a possible candidate one—out of their two nearly equivalent, next low-energetic structures—whose localized, low-temperature states are characterized by the occurrence of charge density waves, thus indicating the presence of electron–phonon interactions.

In the meantime, Mizoguchi reported on a further complication of the low-temperature ordering in Fe_3O_4 , in the form of a higher resolved A-site NMR line pointing to the existence of an additional *ac-glide* plane which, however, is not compatible with the long-accepted C_C symmetry [193]. In order to master this new complication, he proposes a combination

of charge density waves, along the $\langle 10\bar{1} \rangle$ - and $\langle 01\bar{1} \rangle$ -lines in the (111) plane together with bonding/antibonding interactions between the electron orbitals [252]. Thereby, further interactions are introduced in the form of attractions (due to bonding orbitals near the nodes of charge density waves) and repulsions of Fe ions (due to antibonding orbitals near the loops of charge density waves). This rather complicated orbital ordering is suggested to become stabilized by nearest-neighbour Coulomb forces, causing parallel orientation of the Fe ion orbitals with respect to the bonding orbitals.

(2) *Ionic low-temperature order: Queries and MAE-based confirmation.* In contrast to the rather sophisticated Mizoguchi ordering scheme, Novak *et al* [253], on the basis of their high-resolution NMR studies on BRA-quality single crystals, come to remarkably different conclusions, leading them to finally question the existence of any low-temperature ionic ordering at all. There is no doubt of low-temperature electron localization, however, since in agreement with C_C crystal symmetry they are able to resolve, over the temperature range $4.2 \text{ K} < T < T_v$, eight A-type and 16 B-type lines. On crossing T_v to higher temperatures all lines of a given type coalesce into one line, thus leaving—due to *motional narrowing*—a reduced spectrum of only two residual lines (cf section 3.2.4). From this observation they conclude straightforwardly that SRO above T_v is either completely absent or, if still existent, fluctuating at a rate above the NMR frequency (of about $\nu \simeq 10^8 \text{ s}^{-1}$). By analogy with the spontaneous break-down of the MAE above T_v (cf section 3.2.4(3)) and with confidence in the well corroborated Anderson condition, we suggest intensified fluctuations ($\tau < 10^{-8} \text{ s}$) to cause the reduction or complete suppression of the NMR and MAE spectra for $T > T_v$.

Another puzzling finding of Novak *et al* is the observation of nearly coincident spin–lattice relaxation times T_1 for all (A- and B-type !) resonance lines. *A priori*, one would expect the Fe^{2+} ions to relax with a considerable shorter T_1 due to their stronger coupling to the lattice via their—in contrast to Fe^{3+} ions—non-zero spin–orbit interaction. Novak *et al* interpret their result in terms of strongly intermixed, localized Fe^{2+} (B) and Fe^{3+} (B) configurations, allowing even at lowest temperatures fast electron exchange, on a timescale of $\tau < 10^{-8} \text{ s}$, which would (i) explain the coincidence of T_1 for all ions but—in their opinion—also (ii) destroy the conception of a stable, low-temperature ionic order. This second conclusion immediately found a positive echo by Garcia *et al* [254], who in their x-ray resonant scattering studies [SSC (A), 90 K/SSC (B), 120 K] observed no change in the reflections upon crossing T_v and consequently also postulate, by referring to Novak *et al*, the absence of any charge ordering in the low-temperature phase of perfect Fe_3O_4 . These conclusions, [253] and [254], however, are not supported by MAE experiments [120–125, 185, 195], cf section 4.2.3, which clearly prove the existence of definitely distinguished Fe^{2+} and Fe^{3+} ions with lifetimes to be guessed, by the mere occurrence of their associated pronounced low-temperature MAE spectra to, at least, $\tau > 35 \text{ s}$ [15–17].

Concordance between the diverging NMR and MAE results may be obtained by differing between two modes of low-temperature tunnelling: (i) coherent and (ii) incoherent, being characterized by completely different timescales. Whereas the MAE is sensitive only to thermally-activated incoherent tunnelling inside the domain walls, occurring within the regime of seconds (or even minutes cf sections 3.2.4(3), 3.3.2(3) and 4.2.3), coherent tunnelling between different valent ions in the bulk takes place within intervals of $< 10^{-9} \text{ s}$. Thus, it is suggestive to explain the—seemingly—negative result in NMR (lacking T_1 discrimination between Fe^{2+} and Fe^{3+} ions) by rapid valency exchange of Fe^{2+} ions, according to equation (1), in order to avoid their—in comparison to spin–orbit-interaction free Fe^{3+} ions—rather energy-expensive spin-orientation under the action of induced NMR pulses. In this respect, formally Novak *et al* are right in assuming valency fluctuations to be responsible for the failure of

discriminating, by means of T_1 , between Fe^{2+} and Fe^{3+} ions. These fluctuations, however, are not the primary cause of this obvious failure but rather a secondary system-reaction on the conduction of their experiments. In truth, this failure may even be regarded as proof for the existence of an ionically ordered phase, since such an ordered state is prerequisite for fast *coherent* low-temperature tunnelling. For instance, in MAE experiments, being confined on the ‘disturbed’ lattice zones within the domain walls, it is only by relatively slower *incoherent* tunnelling that Fe^{2+} ions are able to energetically rearrange in the low-temperature phase.

Various aspects are to be considered in order to qualify the negative low-temperature results of x-ray scattering [254]: (i) this technique is known to respond (at room temperature) to the various Fe valency states in the specific oxide compounds FeO (Fe^{2+}), Fe_3O_4 (Fe^{2+} , Fe^{3+}) and Fe_2O_3 (Fe^{3+}) by characteristic shifting of the 7.1196 keV Fe K-absorption edge (relative to FeO) of about 2 and 5 eV, respectively [255]. Based on these results and being aware of the short interaction time of their technique (10^{-16} s), as compared to charge transport processes (minimum of about $\sim 10^{-12}$ s, in the case of coherent tunnelling), Garcia *et al* claim to be, in principle, able to (i) discriminate between Fe^{2+} and Fe^{3+} ions in the Anderson SRO state above T_v and (ii) resolve the SRO–LRO transition upon cooling below T_v by means of modified K-edge shifting. From the absence of corresponding effects in their experiments they conclude, consequently from their point of view, (i) the non-existence of Anderson SRO above T_v and (ii) absence of any type of ionic ordering below T_v . None of these conclusions is tenable, however: (i) since their x-ray reflections (above T_v) must be regarded as a mean value obtained over many ions, all that can really be expected, concerning the Anderson SRO, is an intermediate K-edge shifting, averaging over the contributions of both Fe^{2+} (0 eV) and Fe^{3+} -ions (5 eV). Thus, the observed K-edge shifting of about 2 eV in Fe_3O_4 , by Sasaki [255], may be regarded as direct confirmation of an existing Anderson SRO above T_v . (ii) Although the quantitative effect of LR ordering, below T_v , on the observed x-ray spectrum is unknown, it may be guessed to be considerably smaller than the difference of about 2 eV between the separated systems Fe_3O_4 and FeO or Fe_2O_3 , respectively. The fact that Garcia *et al* [254] do not find any relevant difference¹³ in the absorption spectra of their two qualitatively considerably differing crystals A [SSC, 90 K !] and B [SSC, 120 K] sheds some doubts on the resolution power of their technique with respect to the expected effects of charge localization and ionic ordering below T_v , even in the relatively higher-quality crystal B.

Whatsoever, the occurrence of clearly defined, pronounced MAE spectra in the low-temperature range ($T < T_v$) of Fe_3O_4 are a clear indication that there exist distinguishable, differently valent, localized ionic states whose order configurations may be regarded as stable over times of (at least) not shorter than the characteristic time-intervals of our MAE measurements (i.e. of the order of some minutes). On the reliable basis of these observations, all doubts in the presence of clearly distinguishable localized, differently valent ionic order states in the low-temperature phase of magnetite may be regarded as rather speculative, as shown in the foregoing.

¹³ Of these two samples, when subdued to MAE spectroscopy, crystal B of medium-quality should display only moderately altered ionic-order induced low-temperature spectra ($4 \text{ K} < T < 35 \text{ K}$; $50 \text{ K} < T < 125 \text{ K}$)—whose appearance is bound to the existence of well arranged, localized Fe^{2+} and Fe^{3+} ions. Conversely, in the rather poor-quality ($T_v \simeq 90 \text{ K}$!) crystal (A) these low-temperature MAE spectra are expected to be completely suppressed or severely mutilated (cf figure 11(b)) due to impurity-induced destruction of ionic order. The fact that no corresponding difference is perceivable in the resonant x-ray spectra of these two crystals points to a lack of sensitivity in discriminating between the various states of ionic ordering in Fe_3O_4 (i.e. SRO and LRO).

5. Summary and outlook

The present review, covering about 90 years of intensive experimental and theoretical occupation with the electro-magnetic properties of Fe_3O_4 and its Verwey transition at 125 K, shows that especially in recent years (era III), based on well-defined experimental conditions, decisive progress in the understanding of underlying problems could be achieved, as enumerated in the following:

- (1) Finally, it has been possible to furnish the unambiguous proof—against a long-lasting background of uncertainty and speculation—that perfect (*bulk, single crystalline*) magnetite is characterized by only *one, single, first-order* Verwey transition at 125 K.
- (2) In the meantime, there exists wide-spread recognition that further insights into open problems relating to magnetite are obtainable only by means of *bulk, single crystals of perfect stoichiometry*, grown in accordance with optimum preparation rules and phase diagrams. An essential point in this context is the accurate controlling of the oxygen partial pressure, not only during maintenance of the thermodynamic high-temperature equilibrium, but also—*most importantly—during cooling down* to room-temperature. Violation of this precept—by uncontrolled quenching of the specimen, as is often practised at the end of tempering—causes considerable loss of crystal quality, as clearly shown in this report.
- (3) In addition to optimum preparation techniques, careful control of crystal quality is indispensable. The eminent advantages of MAE spectroscopy to this respect have been outlaid in detail. Especially in the low-temperature phase of Fe_3O_4 —where otherwise only rather unspecific results are produced—this technique reacts most sensitively to the smallest deviations from stoichiometry, due to any kind of lattice defects of either intrinsic (internal stresses, vacancies, interstitials, etc) or extrinsic (impurities) type. Thus, in order to rationalize future work, it would be desirable to carefully analyse, prior to experiments, all crystals in the proposed way.
- (4) One may be curious whether on the basis of such optimally prepared and controlled crystals it should not be possible—by careful repetition of respective experiments—to straightforwardly eliminate most of the (too) long-lasting ambiguities concerning crystal symmetry, ionic low-temperature ordering etc.
- (5) On the basis of such well-defined, reliable experimental data, conclusive theoretical concepts for perfect magnetite would be feasible. On retrospection from such a hypothetical basis, the abundant amount of previous results obtained on imperfect magnetite—precise experimental documentation presumed—could be conveniently explained in terms of their respective deficiencies from the ideal crystal state. Accordingly, most of these previous results—although of diminished importance—would continue to be of pedagogical value.
- (6) Concerning theoretical tools, we presently have two promising concepts at hand, going back to Mott and Ihle-and-Lorenz. Of these, roughly speaking, Mott's view of Wigner crystallization below and Wigner glass formation above T_v is in better accordance with *low-temperature* conductivity experiments, especially under the aspects of MAE spectroscopy. The Ihle-Lorenz model, on the other hand—impressive by its explicitly elaborated, well structured formal presentation, accounting in terms of a detailed Hamiltonian for the various interactions between electrons and their lattice surroundings—offers the better quantitative description of the high-temperature conductivity ($T_v < T < 600$ K). These two models do not conform with each other concerning the question of low-temperature polaron-tunnelling which is predicted by Mott—in agreement with low-temperature MAE analyses—as resulting from the formation of *narrow* bands in a Wigner crystal for $T \rightarrow 0$.

On the other hand, Ihle and Lorenz postulate for this condition, perhaps too rigorously, complete band suppression $B \rightarrow 0$, thus ‘offering’ only hopping in this temperature range. However, the Ihle–Lorenz model is also of strong prognostic power, for instance, when suggesting that—to first-order approximation—the Verwey transition and ionic ordering are describable in terms of solely nearest and next-nearest neighbour Coulomb interactions: in agreement with this prediction Brabers *et al* were able to develop a mean-field model permitting surprisingly good quantitative estimations of characteristic system parameters [237–239]. Thus, one aim of future theoretical work could be to find reconciliation between these fruitful Mott- and Ihle–Lorenz conceptions—a task which Mott himself regarded as not unrealistic to solve.

- (7) Recent irritations arising from queries as to the existence of any low-temperature ionic ordering in magnetite at all are refuted in this report on the basis of thorough analyses of MAE results obtained on perfect single crystalline Fe_3O_4 . This is further supported by recent information obtained on e^- -irradiated YIG. On this basis it is shown how recent NMR results—seemingly, on a first *ad hoc* view, in contradiction with low-temperature ionic ordering—under consequent MAE aspects may be interpreted as in full agreement with such order.
- (8) In summarizing our review—spanning three eras, from (I) first experiments to model inauguration (Verwey) over (II) impetuous, large-field activities, not free of considerable error rates to, finally, (III) conscious progressing after reconsideration of optimum strategies (1979 Cambridge conference)—a feeling of optimism seems justified that, in following the spirit of era (III) as documented in this report, we—all together—shall be able in the near future to find conclusive answers to the still unanswered questions on both the experimental and theoretical field.

Acknowledgments

With gratitude I remember numerous fruitful and enlightening discussions with my colleagues Professor Dr H Kronmüller, Dr V A M Brabers and Dr J V H J Brabers during many years, frequently touching questions of the topics presented here. The technical assistance of Mrs Therese Dragon and Mrs Ingrid Schofron in the preparation of this manuscript is highly appreciated. The steady and reliable support of our MPI library team was of invaluable help during literature research—in this connection I remember also with pleasure the additional competent and friendly contribution of Mrs Ursula Zimmermann from the ETH Zürich library.

Appendix. Fundamentals of the MAE spectroscopy

A.1. Underlying principles

As repeatedly outlined in this review, many valuable and frequently decisive results—concerning the Verwey transition and low-temperature conductivity in Fe_3O_4 —have been obtained, since the 1970s (eras (II) and (III)), by means of the MAE spectroscopy. Nevertheless, the general knowledge of this capable technique, especially with respect to the study of the low-temperature phase of Fe_3O_4 , appears to be rather scarce. It therefore may be appropriate to briefly sketch here the outlines of this successful method. The efficiency of MAE spectroscopy as practised in our Stuttgart group is based on two fundamental ideas.

- (1) Full exploitation of the advantageous, *inherent features* of the MAE. These are characterized by (i) the *dynamism* of the method, permitting to obtain information not only on the *stationary presence* of lattice defects and their averaged interactions—to which most

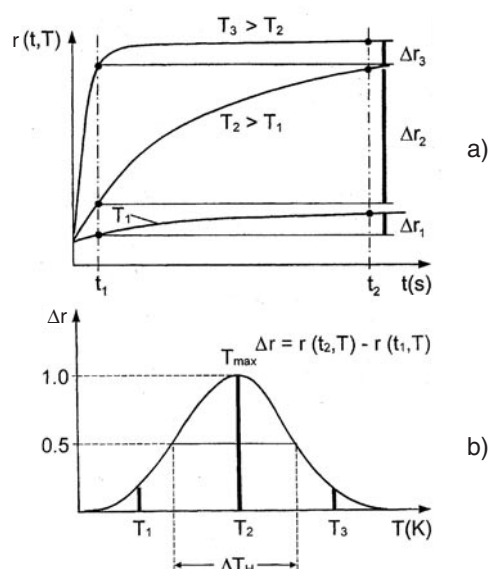


Figure A.1. (a) Isothermal representation of the thermally activated relaxation of the initial reluctivity, $r(t, T)$, for three temperatures $T_1 < T_2 < T_3$ within the time interval of measurements $t_1 \leq t \leq t_2$; (b) construction of an isochronal relaxation curve using the isotherms of (a). T_{\max} : temperature location of the peak maximum; ΔT_H : half-width of the relaxation peak.

other, ‘static’, techniques like resistivity, x-ray and neutron scattering, Mössbauer-effect, etc are confined—but also on their individual *motion modes*, thereby offering the chance of deeper insights and definite discrimination between different defect types [15–17]. (ii) Moreover, this technique is of high *sensitivity* since the three-dimensionally structured domain walls, acting as probes, upon periodically oscillating within their potential wells (figure A.2), are able to interact with large numbers of lattice defects, thereby producing pronounced measuring effects. (iii) Further advantages of the MAE consist in the ease of its application (just putting a sample into a solenoidal coil) and the availability of wide temperature ranges ($4 \text{ K} < T < 1000 \text{ K}$) for the study of defect relaxations and reactions [15–17].

- (2) Refined automatization of the data acquisition. In order to obtain full information on time- and temperature dependent defect reactions, isothermal relaxation measurements are to be made, usually over wide temperature ranges. As discussed later, such measuring programs are rather time consuming, extending often over several days or even weeks. Evidently, the performance of measuring series of such lengths is impracticable by means of conventional MAE methods (manually operated bridge systems). We therefore developed a highly-sensitive, completely automated MAE technique, based on a modern electronic LC-oscillator circuit, permitting direct digital data acquisition and subsequent numerical analysis [16]. The ingenious combination of the information-rich physical magnetic after-effect with modern digital electronics results in a most effective means for the detection and identification of mobile lattice defects like small polarons in the present case or, as outlined in a previous review on metallic α -iron [17], of irradiation-induced intrinsic and/or impurity defects.

A.2. Formal description of the MAE

The demagnetization of a ferro- or ferrimagnetic sample is usually followed by a time-dependent decrease of the initial susceptibility, χ , being caused by a stabilization of the domain walls in the sample. This phenomenon is referred to as a disaccommodation of χ , or more appropriately, a disaccommodation of the initial reluctivity, r —defined as the reciprocal of χ , i.e. $r = 1/\chi$. The observed decrease of $\chi(t, T)$ —or increase of $r(t, T)$ —at constant temperature is known as isothermal relaxation whose strength, in the case of a thermally activated process, may be strongly temperature-dependent, as shown in figure A.1(a). Whereas such *isothermals* are useful for a study of the *time-dependence*, *isochronal* curves in figure A.1(b) are more appropriate for analysing the *temperature dependence* of a given MAE and separating it from other overlapping processes.

In figure A.1, an isochronal curve is constructed, exemplarily, from the maximum amplitudes of three isothermals obtained by measuring—immediately after demagnetization at t_1 , up to the maximum observation time t_2 —at three characteristic temperatures T_1 , T_2 and T_3 , using the relation:

$$\Delta r(t_1, t_2, T) = r(t_2, T) - r(t_1, T). \quad (\text{A.1})$$

In the case of a thermally activated process, the resulting isochronal relaxation curve exhibits a pronounced maximum, as qualitatively shown in the following way: at the low-end temperature T_1 , the relaxation occurs so slowly that within the time-interval $(t_2 - t_1)$ almost no relaxation takes place. At the high-end temperature T_3 , the relaxation proceeds so fast that thermal equilibrium is attained before the measurement starts at t_1 . Between these extremal temperatures, a medium temperature T_2 exists which is characterized by a maximum relaxation amplitude within the observation time. Consequently, the characteristic parameters of an isochronal relaxation maximum consist of (i) its temperature position, T_{\max} , being related to the relaxation time $\tau(T)$ which, in the case of a thermally activated process, follows the Arrhenius equation

$$\tau(T) = \tau_0 \cdot \exp(Q/kT) \quad (\text{A.2})$$

with τ_0 an atomistic jump time and Q the activation enthalpy; (ii) the halfwidth of the relaxation maximum ΔT_H —which, when exceeding the breadth of the ideal process, points to a corresponding distribution of activation enthalpies, ΔQ ; and (iii) the amplitude of the relaxation strength, $\Delta r(T_{\max})$. Only the latter parameter depends on the number of process-participating defects and therefore can be used for a quantitative determination of the defect content [256].

A.3. The LC-oscillator measuring technique

In terms of a micromagnetic picture, the domain walls, prior to demagnetization, lie at the bottom of potential wells and relaxation phenomena—induced by a delocalization of the walls during demagnetization—may be explained by a deepening of these wells due to a time-dependent component ϕ_t in the total potential, $\phi_{\text{tot}} = \phi_t + \phi_0$, cf figure A.2. Whereas ϕ_t accounts for the relaxation due to *mobile* lattice defects, ϕ_0 results from interactions of the domain walls with all defects being *immobile* in the observed temperature range. In ac-experiments, where a small alternating magnetic field of constant amplitude causes the wall to oscillate about its equilibrium position, the deepening of the potential wells leads to a time-dependent decrease of the wall mobility, as qualitatively shown in figure A.2: immediately after demagnetization ($t = 0$) the wall will be displaced by the amount $\overline{AA'}$, whereas somewhat later ($t > 0$) the corresponding displacement is reduced to $\overline{BB'}$. This decreasing wall mobility causes

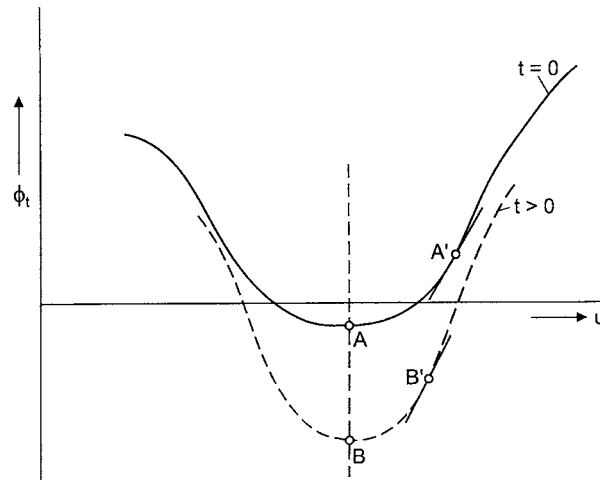


Figure A.2. Reduction of the domain wall mobility due to a time-dependent deepening of the potential well in the course of a magnetic after-effect.

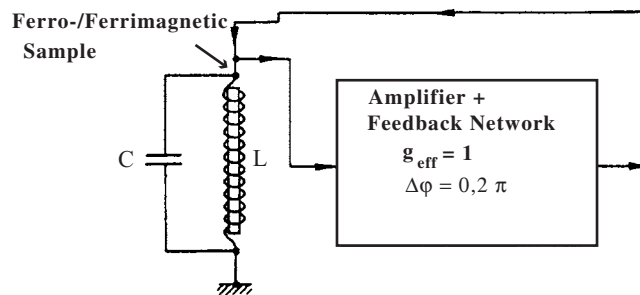


Figure A.3. General principle of the feedback LC-oscillator circuit used in our automated MAE technique; g_{eff} , effective gain and $\Delta\varphi$ input/output phase relation as adjusted by the control circuit, cf [257].

a reduction of the initial permeability, $\mu = \chi + 1$ (SI units), and an increase of the initial reluctivity, r , which allows direct access to a theoretical process analysis in terms of the time-dependent (t_1, t_2), isothermal, interaction potential Φ (figure A.2):

$$\Delta r(t_1, t_2)_T = r(t_2) - r(t_1) = A(g, M_S, S) \left\{ \frac{d^2\Phi(t_2)}{dt^2} - \frac{d^2\Phi(t_1)}{dt^2} \right\} \quad (\text{A.3})$$

with the coefficient A depending on geometrical structure, g , saturation magnetization, M_S , and, surface S , of the domain-wall.

The basic principle of our MAE technique consists in measuring such permeability variations by means of an LC-circuit, whose inductivity is formed by a solenoidal coil containing, as core, the ferri- or ferromagnetic sample under investigation [16]. Realizing appropriate feedback, as thoroughly discussed in [257] and indicated here by the 'black box' in figure A.3, this circuit is kept continuously oscillating with small amplitudes, corresponding

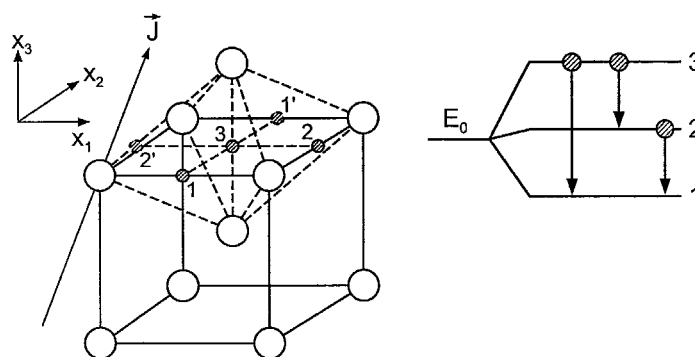


Figure A.4. Possible locations of interstitially dissolved C atoms in the lattice of α -Fe, together with a qualitative energy level diagram of respective positions—as described in the text.

to some few mOe, and resonance frequencies in the 1 kHz range. Via the Thomson formula,

$$\omega^2 = \frac{1}{LC} = \frac{1}{(\mu_r \mu_0 L_0) \cdot C} \quad (\text{A.4})$$

expressed in terms of the circuit parameters L , C — L , resulting from loading the empty coil L_0 with a sample of relative permeability μ_r ; μ_0 , magnetic field constant (SI system) and C , the capacity—process-induced variations of the permeability entail corresponding variations of the oscillator eigen-frequency which can be resolved to an accuracy of about 10^{-5} by means of a digital frequency counter. This digital data acquisition offers the key for the convenient automatization of the complete measuring process. Under the realistic assumption $\mu_r \gg 1$, the relation $\mu_r \simeq \chi_r = 1/r$ holds, permitting a parameter-free formulation of the relative reluctivity in terms of the corresponding oscillator frequencies, ν_i :

$$\frac{r(t_2) - r(t_1)}{r(t_1)} = \frac{\Delta r}{r_1} = \frac{\nu_2^2 - \nu_1^2}{\nu_1^2}. \quad (\text{A.5})$$

Relation (A.5), in combination with equation (A.3) offers, evidently, a convenient bridge for the theoretical interpretation and analysis of the experimental data.

A.4. Classical example illustrating the MAE technique

The classic example *par excellence* for the demonstration of a Debye-type, thermally activated relaxation process is the so-called Richter-MAE of carbon (C) in α -iron (α -Fe) [258]—i.e. the magnetic analogon of the well-known mechanical Snoek effect [259]. As shown in figure A.4, C atoms dissolve interstitially in the α -Fe lattice on the centres of elementary cube edges, i.e. in positions of tetragonal symmetry. Thus, the impurity-induced anisotropy is directed along the line joining two next-nearest Fe neighbours, i.e. oriented in a $\langle 100 \rangle$ direction. From first inspection, one might assume—like Snoek did initially [259]—that, due to magnetostrictive interactions, these elementary anisotropies would try to align themselves in parallel with the spontaneous magnetization \vec{J} . Néel, however, was able to show that, in fact, magnetocrystalline interactions play the dominant role in this relaxation [260] so that those $\langle 100 \rangle$ cube edges enclosing the *largest* angles with the spontaneous magnetization are energetically privileged, cf figure A.4. Immediately after demagnetization the starting conditions are such that a domain wall finds itself in a position where all defect orientations are equally populated. The interstitials, however, will start jumping, via thermal activation, so as to minimize the interaction energy by predominantly populating the privileged cube

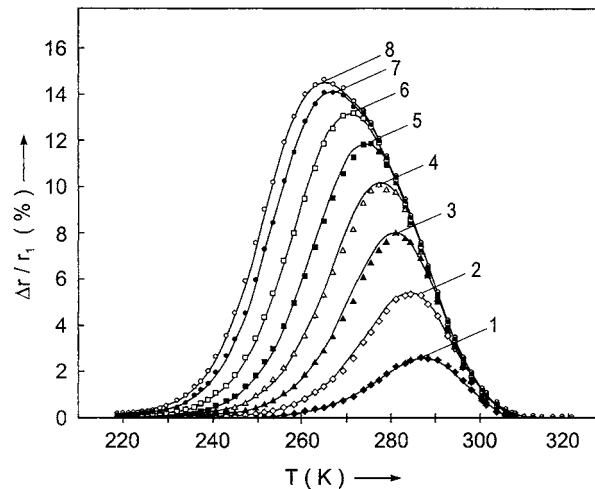


Figure A.5. The classic C-Richter MAE spectrum in α -Fe, resolved by means of the LC-oscillator technique, as described in the text. The various isochronals are characterized by the following time parameters: $t_1 = 1$ s; (1) $t_2 = 2$ s, (2) 4 s (3) 8 s, (4) 16 s, (5) 32 s, (6) 64 s (7) 128 s, (8) 180 s.

edges (figure A.4). This leads to a lowering of the potential ϕ_t (figure A.2) and thus, as described, to an increase of the initial reluctivity and hence to the respective MAE. Figure A.5 shows—as prototype for a simply thermally activated, Debye-type relaxation process—the characteristic maximum resulting from the reorientation of interstitially dissolved C in α -Fe. The experimental data were obtained under the standard conditions for our MAE experiments, i.e. at temperatures controlled to an accuracy of about 0.01 K during isothermal measurements beginning at $t_1 = 1$ s after demagnetization and continued over the times $t_2 = 2$ s (1), 4 s (2), 8 s (3), 16 s (4), 32 s (5), 64 s (6), 128 s (7) and 180 s (8). These data (symbols in figure A.5) were fitted (continuous curves) using a least-squares technique, described generally in [17] and in [195, 216, 221] under the special aspect of typical relaxations occurring in Fe_3O_4 and related ferrites. The corresponding numerical analysis yielded the following process parameters (cf (A.2)): $Q = 0.84$ eV, $\Delta Q = 0.04$ eV, $\tau_0 = 3 \times 10^{-15}$ s and C-content $C_C \simeq 30$ atppm, cf [17, 256].

A.5 Basic MAE mechanisms in magnetite

As exemplarily outlined for the Snoek–Richter MAE of C in α -iron, MAEs generally may be considered as arising from delayed rearrangements of local—mostly defect-induced—anisotropies due to magnetocrystalline interactions with the spontaneous magnetization in the domain wall. These rearrangements, causing a decrease of the domain wall mobility, are responsible for the macroscopically observable disaccommodation of the initial susceptibility, cf section A.2. Usually such local anisotropies may be induced by a variety of lattice defects, being in type either intrinsic (vacancies, interstitials, dislocations, etc) or extrinsic (substitutionally or interstitially dissolved foreign atoms (C-Richter MAE)), cf [17]. Magnetite, however, is distinguished by *specific* MAE spectra occurring, faultlessly developed to full strength in the low-temperature range $T < T_v \simeq 125$ K, *only* in the case of *completely undisturbed, perfectly stoichiometric* single crystals, cf sections 3.2.4(3), 3.3.2(3) and 4.2.3. This extraordinary behaviour is founded on the valency exchange according to equation (1) which, inherently, is connected with a transport of local anisotropy between the spin-orbitally coupled $\text{Fe}^{2+}(3d^6)$:

6D_4) and zero-orbital $Fe^{3+}(3d^5: {}^6S_{5/2})$ ions. Whereas, evidently, this mechanism is working most efficiently in the undisturbed system, it becomes specifically affected in the presence of any type of lattice defects, as is reflected in correspondingly modified MAE spectra by, i.e., suppression of the original low-temperature spectrum and, possibly, the occurrence of new significant processes in other temperature ranges, cf sections 3.2.4(3), 3.3.2(3) and 4.2.3.

These few remarks highlight the already crucial importance of these unique, intrinsic low-temperature ($T < T_v$) MAE spectra in Fe_3O_4 with respect to sample control and defect analysis in this system, as outlined to a greater extent in the present review.

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