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VIEWPOINT

Is the Verwey transition in Fe_3O_4 magnetite driven by a Peierls distortion?

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Online at stacks.iop.org/JPhysCM/21/271001**Abstract**

In this viewpoint article we analyse recent crucial structural, optical and transport experiments on Fe_3O_4 magnetite across the Verwey transition at $T_V \sim 120$ – 125 K. We find that all the relevant experimental data are consistent with a model of a Peierls distortion in the cubic spinel lattice, and likewise, some of them evidence against the original and still distributed hypothesis of the long range charge ordering origin of the Verwey transition. An estimated Peierls transition temperature (T_P) is comparable with T_V . The Peierls model provides new insight into the electronic properties of magnetite. Application of the Peierls model to some other systems is briefly discussed also.

(Some figures in this article are in colour only in the electronic version)

At ambient conditions, magnetite, $\text{Fe}_2^{3+}\text{Fe}^{2+}\text{O}_4$, adopts a cubic spinel structure (space group $Fd\bar{3}m$) with the inverse electronic configuration $[\text{Fe}^{3+}]_A[\text{Fe}^{2+} + \text{Fe}^{3+}]_B\text{O}_4$ [1], where A and B mean respectively the tetrahedral and the octahedral sites in the spinel structure (figure 1); a precise $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio at the B sites still being a point at issue [2, 3]. Below $T_V \sim 120$ – 125 K magnetite exhibits a ‘metal–insulator’ transition (called the Verwey transition (VT)) at which the electrical resistivity abruptly rises by ~ 2 orders of magnitude [4] (figure 2(a)). The first tentative addressing of this transition to ordering of the Fe ions (charges, Fe^{2+} , and vacancies, Fe^{3+}) on the B sites [4, 5] has become commonly adopted. Some charge ordering was in fact experimentally detected in the insulator phase [6–9]. Speculative theoretical models (for example [10–16]) explain in masterly way how this long range charge ordering could drive this ‘metal–insulator’ transition.

On the other hand, it was established that the VT is concurrent with a structural transformation [17–20]. However,

only a tiny hysteresis is noticed in the temperature dependences of the electrical resistivity for direct and return cycles (for example [21]). This circumstance supports a leadership of the electronic transition rather than that of the structural one. Notice that a hysteresis loop may depend on several factors [22, 23], and for instance, in a case of manganites which undergo a transition to a stripe phase a variation in a hysteresis loop was observed [22–24]. Thus, it was believed that magnetite exhibits a unique ‘metal–insulator’ transition which is driven by the enigmatic charge ordering.

Recently, it was shown that a pressure–temperature boundary of the structural transition [25] coincides well with a one for the VT established from electrical resistivity [26, 27]; this challenges the original interpretation of the origin of the VT [4] and calls into being a dispute concerning a driving factor of the VT (electronic or structural) [25]. Another recent study of electrical and galvanomagnetic properties across the VT in fast neutron bombarded magnetite revealed that the disordering leads to only a tiny shift in T_V (figure 2(b)) [28]. This finding gives evidence against the charge ordering

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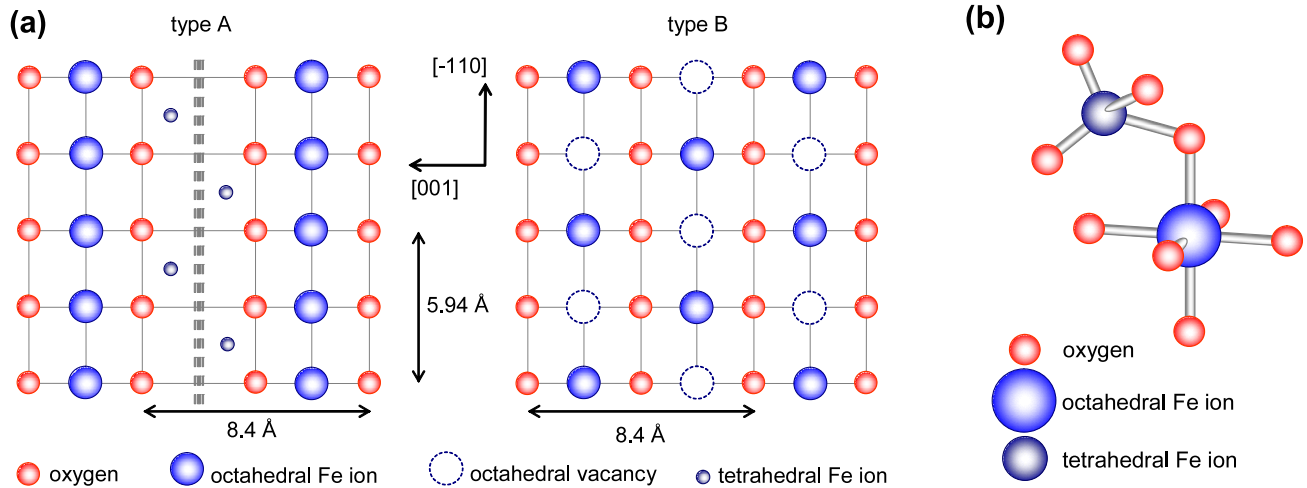


Figure 1. The structure of Fe_3O_4 magnetite may be imagined as a sandwich of two kinds of layers labelled as A and B [21]. The vertical dashed line in (a) shows a demarcation gap in the ‘octahedral lattice’. In (b) a fragment of the structure showing the Fe ions on the tetrahedral and octahedral sites is given [58].

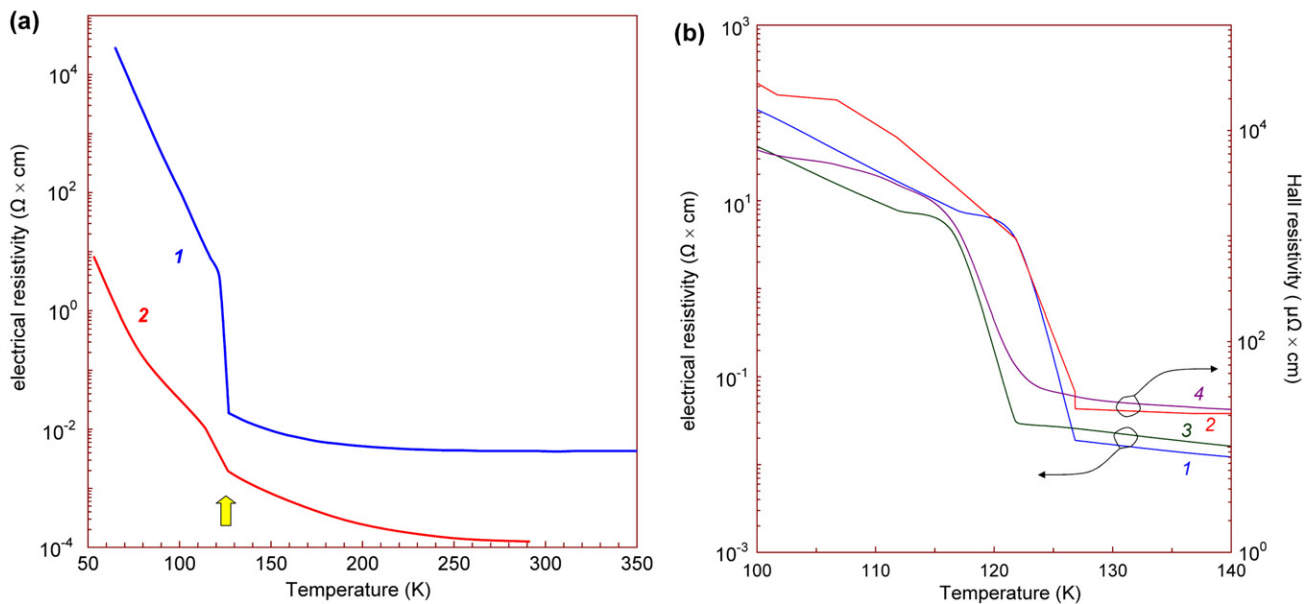


Figure 2. The temperature dependences of the electrical and Hall resistivity of Fe_3O_4 magnetite. Plot (a) shows the ‘metal–insulator’ Verwey transition near $T_V \sim 125$ K (pointed out by the arrow), 1—for a stoichiometric single crystal from [28] and 2—for a thin film from [21]. Plot (b) shows a small decrease in T_V after the fast neutron bombardment (from [28]): 1 and 3—the electrical resistivity and 2 and 4—the Hall resistivity at 13.6 T, before (1, 2) and after (3, 4) the fast neutron bombardment.

mechanism of the VT, while it tolerates a structural one, such as Peierls distortion [29]. Effects of various types of disorder on Peierls transitions have been theoretically considered for 1D [30], 2D and 3D substances [31–33]. For examples of a number of compounds it was derived that the transition weakly depends on a long range ordering, i.e. it can occur in crystalline, amorphous or liquid states [33]. Lattice imperfections and impurities were found to lead primarily to a broadening of the transition [31, 32, 34]. In the case of magnetite the Verwey transition in polycrystalline films is normally smoothed in comparison with the one in single crystals (figure 2(a)). The behaviour of T_V in magnetite under variation in its mesostructure (nanofilms, nanoparticles,

partially amorphous films, etc) is controversial: some works reported a significant decrease in T_V (e.g. down to 80 K [35]) and even non-observation of the VT (i.e. its complete smearing; e.g. [36]), while others found no influence at all (e.g. [37, 38]). This divergence might be related to a very strong dependence of T_V on a nonstoichiometry [39, 40], which is not always properly controlled during sample preparation.

We propose that a Peierls distortion mechanism [29] could explain the VT in Fe_3O_4 . In fact, this model fits well with the known experimental data as follows.

- (i) Below T_V , structural studies revealed a doubling of the cubic unit cell along the c axis as well as a lowering of the symmetry to monoclinic [18–20]. The unit

cell of the Verwey phase was established to consist of four rhombohedrally distorted cells of the cubic phase [8, 14, 41, 42]. Furthermore, it was found that the charge fluctuations of both the iron ions (at the B sites) and the 2p orbitals of the oxygen atoms have a period which is equal to a double lattice constant along the c axis [8, 14, 41, 42].

- (ii) Photoemission spectroscopy experiments established the opening of an energy gap of $\sim 0.05\text{--}0.07$ eV at the VT [43, 44]; the abrupt growth in the electrical resistivity on the VT [4] also hints at the opening of an energy gap.
- (iii) Raman spectroscopy across the VT revealed a dramatic propagation of active phonon modes on the VT: from five at the cubic lattice to thirteen at the Verwey phase [45, 46]. This suggests at least a double folding of the Brillouin zone [45, 46], i.e. a doubling of the lattice parameter.

The aforesaid properties correspond to a basic set of characteristics for Peierls-distortion-driven transitions [29, 47, 48]. Originally, the Peierls distortion mechanism of transitions was established by Peierls for a 1D metal with a half-filled electron band [29]. A lattice distortion with a concurrent doubling of the lattice parameter was shown to be energetically profitable due to opening of a semiconductor gap at the Fermi level and a corresponding lowering of the electron energy [29]. Later, this approach was extended to numerous classes of 2D and 3D structures by consideration of 1D atomic chains along perpendicular X , Y , and Z axes for ‘ideal’ undistorted cubic lattices [47–50]. The model of Peierls distortion is successfully applied for the explanation of physical phenomena in a wide range of 1D–3D materials. For instance, it has demonstrated its efficiency in analysis of: (i) a transition to exotic stripe phases in manganites [22–24], (ii) a heat capacity anomaly in α -uranium [34, 51], (iii) a mechanism of martensitic transition in AuZn alloy with a shape-memory effect [52, 53], (iv) an impurity effect on a magnetic susceptibility in ‘blue bronze’ $\text{K}_{0.3}\text{MoO}_3$ [32], and other engaging phenomena.

A lowering of the electron energy at the Peierls transition is expressed as follows: $\Delta E_{\text{band}} = -\frac{\Delta^2}{W} \ln\left(\frac{W}{\Delta}\right)$, where W is the bandwidth, and Δ is the amplitude of potential for an electron with a wavevector $2k_{\text{F}}$ (k_{F} is the Fermi wavevector) [29, 48]. A Peierls transition occurs when the above ΔE_{band} value exceeds an elastic energy of distortion ($\Delta E_{\text{lattice}} = \frac{1}{2}m\omega^2(u_{k_{\text{F}}})^2$, where $u_{k_{\text{F}}}$ is the displacement amplitude and ω is the LA phonon frequency) [26, 48]. Upon rise in temperature a hopping of carriers over the Peierls gap $E_{\text{g}} = 2\Delta$ decreases the gap value and at a certain temperature $T_{\text{P}} \approx 2\Delta(T = 0)/3.5$ the gap is closed [29]. The estimations performed below show that T_{P} is comparable with T_{V} .

On the VT the charge carrier concentration (n) dropped by ~ 150 times [28]. Likewise, the absolute value of the thermopower $|S|$ increased by a factor of 2–3 [54, 55]. Using the expressions for the thermopower and the concentration as follows: $S = \frac{k}{e} \frac{E_{\text{a}}}{kT}$ and $n = n_0 \exp\left(-\frac{E_{\text{a}}}{kT}\right)$, where E_{a} is the activation energy, k is Boltzmann’s constant, e is the electron charge, and n_0 is the pre-exponential factor (its variation was disregarded) [56], one can estimate the energy gap (E_{a}) at $\sim 0.02\text{--}0.04$ eV. Then, putting $2\Delta = E_{\text{a}}$, the temperature of a Peierls transition is found as $T_{\text{P}} \sim 60\text{--}130$ K, i.e. it is

comparable with $T_{\text{V}} = 120\text{--}125$ K [4]. From photoemission spectroscopy data ($E_{\text{g}} \sim 0.05\text{--}0.07$ eV) [43, 44] the higher values of $T_{\text{P}} \sim 170\text{--}200$ K may be obtained.

Notice that applied pressure of 6–8 GPa abruptly suppresses the VT [26, 27]. This correlates with a circumstance that Peierls-distorted lattices normally have a lowered density and external pressure that exceeds some critical value is able to remove this distortion [33, 47, 50].

Previous studies on Peierls transitions in elemental solids and compounds inferred a dominant role of p electrons in the bonding (the so called ‘p model’) [33, 47, 50]. Thus, p electrons assist in the formation of six rectangular bonds along X , Y , and Z axes at undistorted ‘ideal’ cubic phase (with a simple cubic or rock-salt (NaCl) lattice) [33, 47, 50]. A filling of the p band (e.g. by $\frac{1}{2}$, $\frac{1}{3}$, etc) determines a factor of the lattice enlarging (respectively, by 2, 3, etc times) [33, 47, 48]. The crystal structure of magnetite may be imagined as a rock-salt lattice, in which 50% of sites for Fe atoms are vacant (figure 1(a), right), and furthermore, there are built-in chains of the tetrahedrally coordinated Fe ions and gaps (figure 1(a), left). Thus, the lattice constitutes a 3D rectangular net, which is demarcated in the (110) planes and cross-linked by the tetrahedrally coordinated Fe ions (figure 1). It seems interesting to estimate the population of the general p band of the ‘octahedral lattice’ (i.e. ‘ Fe_2O_4 ’) of magnetite (figure 1) in terms of the ‘p model’ [33, 47]. For the conventional electron configuration of the iron atom ($3d^64s^2$) the p band of the ‘octahedral lattice’ has to be filled with electrons to approximately a half ($\sim \frac{4}{9}$). Iron atoms may have also different configurations, namely, $3d^54s^24p^1$ and $3d^64s^14p^1$ [57]. Then, if the Fe^{3+} and Fe^{2+} ions in ‘ Fe_2O_4 ’ adopt these configurations, the population equals exactly $\frac{1}{2}$; if only the Fe^{3+} ions adopt them, it is $\frac{17}{36}$ [57]. Therefore, the necessary conditions for a Peierls distortion of the lattice are indeed fulfilled.

In summary, we may infer that the Verwey transition in magnetite may be well explained by the Peierls distortion mechanism. Accounting for other recent successive applications of the Peierls model, for instance, for ‘stripy’ phases in manganites [22–24], uranium [34, 51], AuZn [52, 53], and others, one may surmise that the model is more current than they believed earlier. This suggests that the Peierls model may be fruitful for analysis of other materials as well.

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References

- [1] Fleet M E 1981 *Acta Crystallogr. B* **37** 917
- [2] Sasaki S 1997 *Acta Crystallogr. B* **53** 762
- [3] Ovsyannikov S V, Shchennikov V V, Todo S and Uwatoko Y 2008 *J. Phys.: Condens. Matter* **20** 172201
- [4] Verwey E J W 1939 *Nature* **144** 327

- [5] Mott N F 1974 *Metal-Insulator Transitions* (London: Taylor and Francis)
- [6] Huang D J, Chang C F, Jeng H T, Guo G Y, Lin H J, Wu W B, Ku H C, Fujimori A, Takahashi Y and Chen C T 2004 *Phys. Rev. Lett.* **93** 077204
- [7] Goff R J, Wright J P, Attfield J P and Radaelli P G 2005 *J. Phys.: Condens. Matter* **17** 7633
- [8] Huang D J, Lin H J, Okamoto J, Chao K S, Jeng H T, Guo G Y, Hsu C H, Huang C M, Ling D C, Wu W B, Yang C S and Chen C T 2006 *Phys. Rev. Lett.* **96** 096401
- [9] Nazarenko E, Lorenzo J E, Joly Y, Hodeau J L, Mannix D and Marin C 2006 *Phys. Rev. Lett.* **97** 056403
- [10] Jeng H T, Guo G Y and Huang D J 2004 *Phys. Rev. Lett.* **93** 156403
- [11] Leonov I, Yaresko A N, Antonov V N, Korotin M A and Anisimov V I 2004 *Phys. Rev. Lett.* **93** 146404
- [12] Leonov I and Yaresko A N 2007 *J. Phys.: Condens. Matter* **19** 021001
- [13] Brabers J H V J, Walz F and Kronmuller H 1999 *J. Phys.: Condens. Matter* **11** 3679
- [14] Wright J P, Attfield J P and Radaelli P G 2001 *Phys. Rev. Lett.* **87** 266401
- [15] Pinto H P and Elliott S D 2006 *J. Phys.: Condens. Matter* **18** 10427
- [16] Piekarczyk P, Parlinski K and Oles A M 2006 *Phys. Rev. Lett.* **97** 156402
- [17] Hargrove R S and Kundig W 1970 *Solid State Commun.* **8** 303
- [18] Yamada T, Suzuki K and Chikazumi S 1968 *Appl. Phys. Lett.* **13** 172
- [19] Samuelsen E J, Bleeker E J, Dobrzynski L and Riste T 1968 *J. Appl. Phys.* **39** 1114
- [20] Shirane G, Chikazumi S, Akimitsu J, Chiba K, Matsui M and Fujii Y 1975 *J. Phys. Soc. Japan* **39** 949
- [21] Maris G, Shklyarevskii O, Jdira L, Hermsen J G H and Speller S 2006 *Surf. Sci.* **600** 5084
- [22] Cox S, Singleton J, McDonald R D, Migliori A and Littlewood P B 2008 *Nat. Mater.* **7** 25
- [23] Cox S, Singleton J, McDonald R D, Migliori A and Littlewood P B 2009 *Physica B* **404** 433
- [24] Cox S, Lashley J C, Rosten E, Singleton J, Williams A J and Littlewood P B 2007 *J. Phys.: Condens. Matter* **19** 192201
- [25] Rozenberg G K, Pasternak M P, Xu W M, Amiel Y, Hanfland M, Amboage M, Taylor R D and Jeanloz R 2006 *Phys. Rev. Lett.* **96** 045705
- [26] Todo S, Takeshita N, Kanehara T, Mori T and Mori N 2001 *J. Appl. Phys.* **89** 7347
- [27] Mori N, Todo S, Takeshita N, Mori T and Akishige Y 2002 *Physica B* **312** 686
- [28] Shchennikov V V, Ovsyannikov S V, Karkin A E, Todo S and Uwatoko Y 2009 *Solid State Commun.* **149** 759–62
- [29] Peierls R E 1955 *Quantum Theory of Solids* (Oxford: Oxford University Press)
- [30] Lee P A, Rice T M and Anderson P W 1973 *Phys. Rev. Lett.* **31** 462
- [31] Chandra P 1989 *J. Phys.: Condens. Matter* **1** 3709
- [32] Chandra P 1989 *J. Phys.: Condens. Matter* **1** 10067
- [33] Gaspard J P, Marinelli F and Pellegatti A 1987 *Europhys. Lett.* **3** 1095
- [34] Cox S, Rosten E, McDonald R D and Singleton J 2007 *Phys. Rev. Lett.* **98** 249701
- [35] Schneeweiss O, Zboril R, Pizurova N, Mashlan M, Petrovsky E and Tucek J 2006 *Nanotechnology* **17** 607
- [36] Ramos A V, Moussy J B, Guittet M J, Bataille A M, Gautier-Soyer M, Viret M, Gatel C, Bayle-Guillemaud P and Snoeck E 2006 *J. Appl. Phys.* **100** 103902
- [37] Chapline M G and Wang S X 2005 *J. Appl. Phys.* **97** 123901
- [38] Tiwari S, Prakash R, Choudhary R J and Phase D M 2007 *J. Phys. D: Appl. Phys.* **40** 4943
- [39] Kakol Z and Honig J M 1989 *Solid State Commun.* **70** 967
- [40] Shepherd J P, Aragon R, Koenitzer J W and Honig J M 1985 *Phys. Rev. B* **32** 1818
- [41] Iizumi M, Koetzle T F, Shirane G, Chikazumi S, Matsui M and Todo S 1982 *Acta Crystallogr. B* **38** 2121
- [42] Zuo J M, Spence J C H and Petuskey W 1990 *Phys. Rev. B* **42** 8451
- [43] Chainani A, Yokoya T, Morimoto T, Takahashi T and Todo S 1996 *J. Electron Spectrosc. Relat. Phenom.* **78** 99
- [44] Park J H, Tjeng L H, Allen J W, Metcalf P and Chen C T 1997 *Phys. Rev. B* **55** 12813
- [45] Gasparov L V, Arenas D, Choi K Y, Guntherodt G, Berger H, Forro L, Margaritondo G, Struzhkin V V and Hemley R 2005 *J. Appl. Phys.* **97** 10A922
- [46] Gasparov L V, Tanner D B, Romero D B, Berger H, Margaritondo G and Forro L 2000 *Phys. Rev. B* **62** 7939
- [47] Volkov B A, Pankratov O A and Pakhomov C B 1984 *JETP* **86** 2293
- [48] Friend R H and Yoffe A D 1987 *Adv. Phys.* **36** 1
- [49] Littlewood P B 1984 Structure and bonding in narrow gap semiconductors *CRC Crit. Rev. Solid State Mater. Sci.* **11** 229
- [50] Ovsyannikov S V, Shchennikov V V, Popova S V and Derevskov A Y 2003 *Phys. Status Solidi b* **235** 521
- [51] Mihaila B, Opeil C P, Drymiotis F R, Smith J L, Cooley J C, Manley M E, Migliori A, Mielke C, Lookman T, Saxena A, Bishop A R, Blagoev K B, Thoma D J, Lashley J C, Lang B E, Boerio-Goates J, Woodfield B F and Schmiedeshoff G M 2006 *Phys. Rev. Lett.* **96** 076401
- [52] McDonald R D, Singleton J, Goddard P A, Drymiotis F, Harrison N, Harima H, Suzuki M-T, Saxena A, Darling T, Migliori A, Smith J L and Lashley J C 2005 *J. Phys.: Condens. Matter* **17** L69
- [53] McDonald R D, Goddard P A, Lashley J, Harrison N, Mielke C H, Singleton J, Harima H and Suzuki M-T 2006 *J. Phys. Chem. Solids* **67** 2100
- [54] Ramasesha S K, Mohan M, Singh A K, Honig J M and Rao C N R 1994 *Phys. Rev. B* **50** 13789
- [55] Kuipers A J M and Brabers V A M 1979 *Phys. Rev. B* **20** 594
- [56] Seeger K 1973 *Semiconductor Physics* (Berlin: Springer)
- [57] Eliashkevich M A 1962 *Atomic and Molecular Spectroscopy* (Moscow: State Publishing House of Physical and Mathematical Literature)
- [58] Friak M, Schindlmayer A and Scheffler M 2007 *New J. Phys.* **9** 1