

Phase Transitions in Oxides Studied by Perturbed Angular Correlation Spectroscopy

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Radioactive atoms located on cation sites in oxide matrices can be used to monitor phase transitions by measuring the electric or magnetic hyperfine interactions by means of Perturbed Angular Correlations spectroscopy. The article illustrates three types of phase transitions studied with ^{111}In tracers and their daughter nuclei ^{111}Cd , namely magnetic, structural and REDOX phase transitions in binary and ternary polycrystalline or single-crystalline oxides. In this context, we also discuss the question of identifying the probes' lattice site(s), the scaling of the Electric Field Gradients in oxides, the influence of the (impurity) probes themselves on the phase transitions, and the occurrence and mechanisms of dynamic interactions. Recent results on ^{111}In in pure and Li-doped In_2S_3 will also be presented.

Key words: Phase Transitions; Oxides; Perturbed Angular Correlations; ^{111}In ; Point Charge Model.

1. Introduction

“A phase transition occurs when there is a singularity in the free energy or one of its derivatives” [1]. The diversity of phase transitions in oxides spans from antiferromagnetic and ferrimagnetic phase transitions, where the sublattice magnetization is the order parameter, to structural phase transitions (atomic displacements) and ferroelectric phase transitions (electric polarization) [2, 3]. Hyperfine interaction methods such as Mössbauer effect, Perturbed γ -ray Angular Correlations (PAC), Nuclear Magnetic or Quadrupole Resonance (NMR, NQR) and Muon Spin Resonance (μSR) are particularly well suited to monitor local magnetic and electric fields and phase transitions associated with them. The present article reports on several types of phase transitions in binary and ternary oxides studied via PAC spectroscopy employing implanted radioactive ^{111}In , $^{111\text{m}}\text{Cd}$ or ^{111}Ag tracers which all feed the 245 keV isomeric state in ^{111}Cd [4].

Some general remarks concerning the use of PAC for studying the hyperfine interactions in oxides and the relevant definitions of the PAC parameters are the content of Section 2. Magnetic phase transitions in binary oxides are discussed in Section 3. In Sect. 4 struc-

tural phase transitions, mainly in perovskite oxides, are reviewed and the scaling of Electric Field Gradients (EFGs) in different classes of oxides is discussed. A few examples of chemical phase transitions are presented in Sect. 5 which also addresses to the role of dynamic hyperfine interactions. Surveys on previous results for ^{111}In -PAC spectroscopy in binary oxides have been given in a number of articles [5 - 9].

2. Methods: Instrumentation and Analysis

Besides the Mössbauer effect, PAC spectroscopy using radioactive ^{111}In tracers is probably the most common hyperfine interaction method using unstable nuclei. This is due to several favorable conditions of these tracers: ^{111}In decays via electron capture with the convenient half-life of $T_{1/2} = 2.83$ d to ^{111}Cd [4]. The decay feeds a two-step γ -cascade involving well resolved γ -radiations of 171 and 245 keV and the hyperfine-sensitive 245 keV $5/2^+$ state, which has a long half-life (85 ns), a precisely known magnetic moment ($\mu = -0.3062 \pm 0.0010 \mu_N$) and a large quadrupole moment ($Q = 0.83 \pm 13$ b). As in Mössbauer spectroscopy, the benefits of PAC [10] lie in its high local sensitivity, which gives access to structures on an atomic scale. As long as the hyper-

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Table I. Components of a PAC laboratorium designed for the study of phase transitions.

PAC set-up	Detectors	Shape	Angles	horiz., vertical	Turbo-pump	T_{\min} (K)	T_{\max} (K)	Specials
1	4 NaI	cylindr.	90°, fixed	h	yes	10	850	Cryo
2	4 NaI	cylindr.	90°, fixed	h	no	R. T.	1350	CO/CO ₂
3	4 NaI	cylindr.	90°, fixed	h	yes	10/250	850	Cryo/Peltier
4	4 BaF ₂	conical	90°, fixed	v/h	yes	1.5/80	450	mobile
5	4 BaF ₂	cylindr.	variable	h	no	R. T.	R. T.	goniometer

fine interaction is constant during the observation time, PAC is able to resolve different (static) probe surroundings. The method has been extended to dynamic processes on the ns time scale [11 - 16]. PAC is able to distinguish between magnetic hyperfine fields, EFGs and superpositions of both. Moreover, it provides information about the orientation of internal fields relative to crystallographic axes. In comparison with Mössbauer spectroscopy, PAC is more favorable at higher temperatures since it does not depend on a Debye-Waller factor. A further advantage is the small number of radioactive tracer atoms necessary (some 10^{12}) which, in general, do not influence the macroscopic properties of the matrix.

The main limitations of PAC derive from

1. the small number of appropriate nuclear probe nuclei available;
2. the necessity to introduce the radioactivity into the sample to be studied;
3. the need to calibrate the observed hyperfine fields; and
4. modifications which the (generally impurity) probe atoms may exert onto the *local* environment, either due to the chemical nature or the electric activity of the probe atoms or, in the case of implantation, radiation damage. For studying phase transitions, the possible changes of the local environment by the probes have to be checked as shown in Sect. 3 with the local relieve of frustration in CuFeO₂ and in Sect. 4 at the spin-Peierls transition in CuGeO₃.

The theory and methodology of PAC have been reviewed in several articles [4, 17, 18]. At the Göttingen laboratory, ¹¹¹In can be either ion-implanted by means of the implanter IONAS [19], diffused into the sample or deposited via evaporation as thin and even sub-mono layers when used in thin film analysis [20]. We have five 4-detector PAC apparatus available, equipped with either 4 cm long, 4 cm in diameter NaI(Tl) or conical or cylindrical BaF₂ scintillators. The temperature range accessible runs from about 10 K (closed-cycle helium cryostat; high vacuum

chamber) to about 1400 K. Here, a chamber of low γ -ray absorption can be operated either under a protective gas atmosphere or with a CO/CO₂ gas mixture to adjust the oxygen activity. For the BaF₂ detector set-up, Bartos et al. [21] developed a fast-fast electronic module, which includes the single channel analyzers, linear amplifiers, and pole-zero timing circuits for all four channels. Hence, this apparatus is small enough to be easily transportable to other facilities such as ISOLDE/CERN or to a liquid-He cryostat [22]. Table I summarizes the features of these instruments.

As usual, the perturbation function for a 90° detector geometry is expressed as

$$R(t) = A_{22}^{\text{eff}} G_2(t) = 2 \frac{N(t, \pi) - N(t, \pi/2)}{N(t, \pi) + 2N(t, \pi/2)},$$

where A_{22}^{eff} denotes the effective angular correlation coefficient of the unperturbed $\gamma\gamma$ cascade in ¹¹¹Cd and $N(t, \theta)$ the perturbed $\gamma\gamma$ coincidence rate between detectors separated by the angle $\theta = \pi$ and $\pi/2$, respectively. In the case of a purely magnetic interaction, the Larmor frequency ω_L is related to the hyperfine field B_{hf} via $\omega_L = \mu_N g B_{\text{hf}}/\hbar$ and is obtained from

$$G_2(t) = \sum_{n=0}^2 S_n \cos(n\omega_L t) \exp(-n\delta t) d(\omega_L; \tau_R).$$

This expression assumes a unique site having a Lorentzian distribution of Larmor frequencies around the centre value ω_L with width δ , and a finite time resolution τ_R of the PAC apparatus contained in the function $d(\omega_L; \tau_R)$. The coefficients S_n depend on the single- or poly-crystalline form of the sample. The extension to several sites is straightforward. The corresponding expression for a static electric quadrupole interaction is

$$G_2(t) = \sum_{n=0}^3 s_{2n}(\eta) \cos[g_n(\eta)\nu_Q t] \exp[-g_n(\eta)\delta t] \cdot d(g_n(\eta)\nu_Q; \tau_R),$$

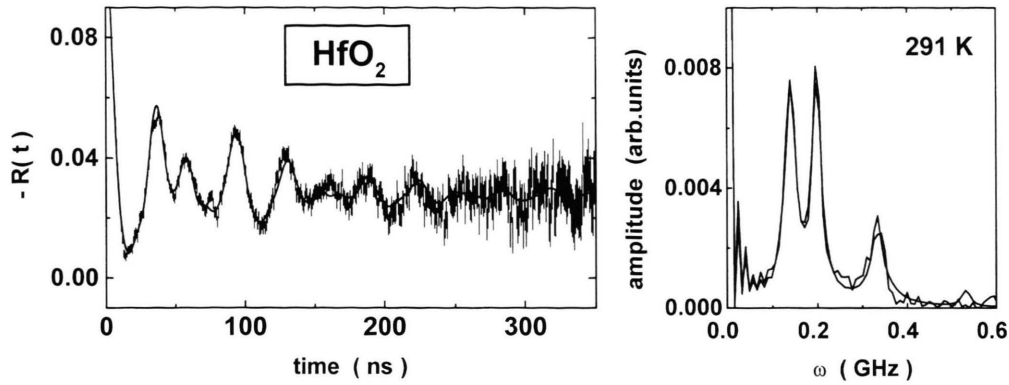


Fig. 1. PAC spectrum (left) and Fourier transform (right) taken at the measuring temperature $T_m = 291$ K after ^{111}In implantation in HfO_2 [32]. The measured EFG is attributed to ^{111}Cd on substitutional, defect-free cation sites.

where the quadrupole coupling constant ν_Q is defined as $\nu_Q = eQV_{zz}/h$. The EFG tensor has the principal axis components $\{V_{xx}, V_{yy}, V_{zz}\}$ and thus can be defined by its largest component V_{zz} and its asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. The coefficients $s_{2n}(\eta)$ and $g_n(\eta)$ are tabulated in [23, 24] for poly- or monocrystalline samples. The term $\exp[-g_n(\eta)\delta t]$ accounts for a distribution of the EFG tensor of width δ at the well-defined η -value. Approximative expressions for $G_2(t)$ in the case of a small hyperfine field B_{hf} superimposed to a large EFG or *vice versa* have been derived e. g. by Wenzel et al. [25] and Raether et al. [26].

A general problem of PAC concerns the lattice site location(s) after implantation and the possible role of radiation damage. Originally, this problem was considered as the main obstacle for applying PAC in oxides, indeed. Our experience after implanting 400-keV $^{111}\text{In}^+$ ions at room temperature into a large number of oxides is that thermal annealing of the sample in oxygen or air at some 1000 - 1700 K for several hours in general leads to removal of almost all radiation damage. In case of existence of higher oxide phases, the annealing was carried out under a protective gas or in vacuum. So far we have performed ^{111}In -PAC studies in more than 35 binary oxides [27 - 33] and 20 ternary oxides of perovskite, cuprate and delafossite structure [34 - 40] and found good evidence that in all cases large fractions of the probe atoms reached substitutional, defect-free implantation sites. As an example, we show in Fig. 1 the perturbation spectrum and Fourier transform obtained by Luthin et al. [32] after ^{111}In implantation into HfO_2 and a 4h-annealing at 1643 K in air. The spectra clearly exhibit the sub-

stitutional EFG for $^{111}\text{In}/^{111}\text{Cd}$ on Hf sites as proven by comparison with PAC results on HfO_2 using the self-atom $^{181}\text{Hf}/^{181}\text{Ta}$ (see Refs. in [32]). In several cases, REDOX phase transitions during the annealing process were observed to dramatically enhance the fraction ascribed to substitutional, defect-free sites in that oxide formed during the phase transition. In these cases, one may implant the probes into an oxygen-poorer phase and oxidize it further to the desired oxide matrix during annealing in air. A convincing example will be presented in Section 5.

3. Magnetic Phase Transitions in Oxides

Oxides offer a large variety of magnetic phase transitions which have been studied *in extenso* via magnetometry, magneto-optical Kerr effect, neutron diffraction, Mössbauer effect [41], Nuclear Magnetic Resonance, muon Spin rotation, and other methods. PAC measurements are sensitive to the temperature variation of the magnetic hyperfine field(s) and therefore allow one to determine the critical parameters such as the phase transition (Néel) temperature T_N and critical exponent β [42]. We have carried out PAC studies with implanted ^{111}In probes e. g. for investigating the antiferromagnetic and ferrimagnetic ordering of Mn_{1-x}O , Fe_{1-x}O , CoO , NiO , CuO , $\alpha\text{-Fe}_3\text{O}_4$ and Co_3O_4 [43 - 49]. On the basis of their non-cubic structures, several of these compounds exhibit one or several EFGs, leading to a combined magnetic/electric hyperfine interaction *below* T_N and a purely electric interaction *above* T_N .

Figure 2 shows the temperature variation of B_{hf} obtained for ^{111}Cd in the anti-ferromagnet CoO [43].

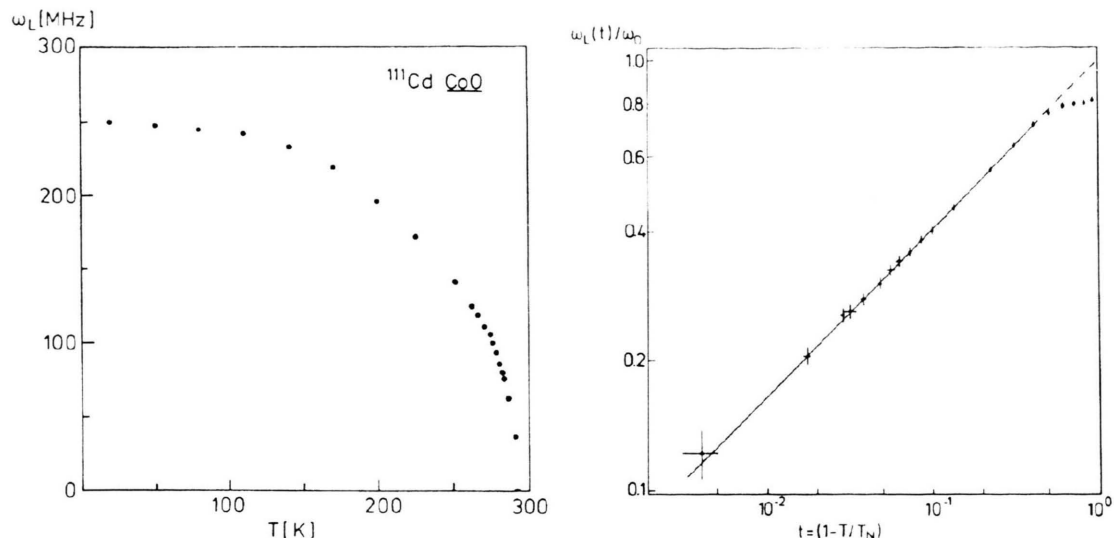


Fig. 2. Temperature variation (left) of the Larmor frequency for ^{111}Cd in CoO [43]. It follows a Curie-Weiss dependence with the critical parameters $T_N = 291.3(3)$ K and $\beta = 0.392(5)$ (right).

Table II. Critical parameters obtained from ^{111}In -PAC spectroscopy for phase transitions in transitional metal oxides.

Matrix	β	T_N	$\omega(0)$ (MHz)	t_{\min}^b	t_{\max}^b	Ref.
Mn_{1-x}O	0.24(1)	88(2)	283(2)	0.001	0.65	[47, 48]
Fe_{1-x}O	^a					[46]
CoO	0.393(5)	291.3(3)	307(2)	0.004	0.4	[42, 44]
NiO	0.385(15)	543(2)	325(5)	0.0013	0.5	[5]
CuO	0.333(10)	223(2)	35(8)	0.002	0.07	[43, 48]
Fe_3O_4	0.392(2) _A	848(2)	204(1)	0.0035	0.65	[45]
	0.392(2) _B			0.0035	0.14	
	0.39(1) _A			0.004	0.02	[59]
	0.41(1) _B					
Co_3O_4	0.34(2) _A	39(1)	112(2)	0.001	0.077	[45, 48]

^a No Larmor precession in AF Fe_{1-x}O observed, probably due to a large deviation x from stoichiometry.

^b The Curie-Weiss relation extends in the interval (t_{\min}, t_{\max}) , where $t = T/T_N$.

Due to the NaCl structure of this oxide, the EFG vanishes. The normalized Larmor frequency $\omega_L(T)/\omega_L(0)$ was found to follow a Curie-Weiss relationship $\omega_L(t)/\omega_L(0) = t^\beta$ with $t = 1 - T/T_N$, $T_N = 291.2(3)$ K and $\beta = 0.393(5)$, over the range $t = 0.004$ to 0.4. The critical parameters T_N and β have also been obtained for the transitional metal monoxides NiO and Mn_{1-x}O and for the inverse spinels Fe_3O_4 and Co_3O_4 (see Table II). In most cases, the β -values are very close to the one expected for 3D-Heisenberg spin ordering, $\beta_H = 0.385$. A rather detailed discussion of Mn_{1-x}O , CuO, and Co_3O_4 was given by Wiarda et al. [48] and Bartos et al. [44, 49].

Comprehensive PAC studies of radiation-induced and intrinsic defects in CoO and NiO were carried

out by Wenzel, Lieb, and Uhrmacher [25, 50]. In these measurements, taking PAC spectra below and above the respective Néel temperatures was essential to determine the fractions of probe nuclei on defect-free substitutional cation sites which, due to the cubic structure of these oxides, do not give rise to an electric quadrupole interaction. Two defect complexes featuring the same critical exponent, $\beta = 0.39(1)$, as the defect-free fraction, but a different Néel temperature of $T_N = 505(2)$ K were identified in NiO [25].

While the cubic structure of the transitional-metal monoxides leads to a purely magnetic interaction, combined magnetic / electric interactions occur in the inverse spinels Co_3O_4 and Fe_3O_4 [46], below the respective Néel temperatures. These circumstances

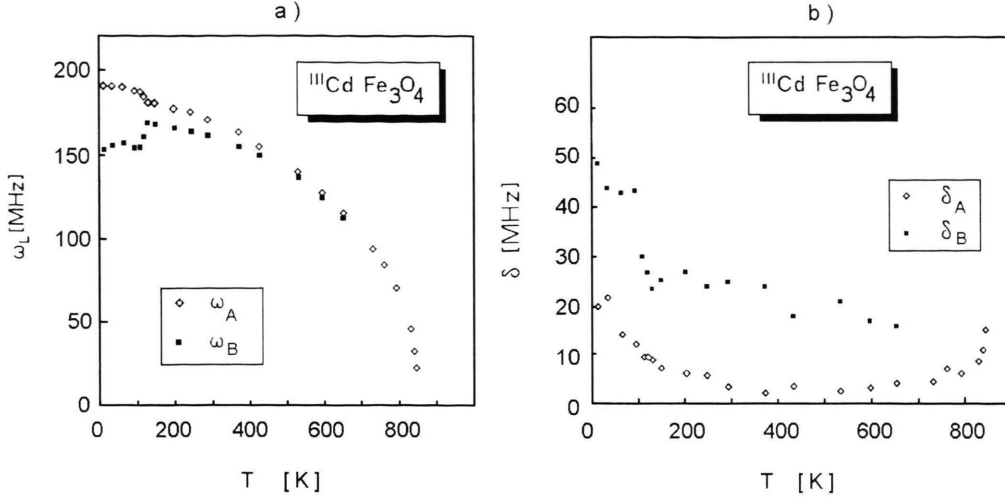


Fig. 3. Temperature variations of a) the Larmor frequencies $\omega_{L,A,B}$ and b) width parameters $\delta_{A,B}$ for ^{111}Cd at the tetrahedral A site and octahedral B site in the inverse spinel Fe_3O_4 , showing the ferrimagnetic phase transition at $T_N = 848$ K and the Verwey transition around $T_V = 125$ K [46, 54].

limit the accessible temperature range and may lower the precision of the deduced critical parameters (see Table II). As an example, Fig. 3a illustrates the temperature dependence of the Larmor frequencies ω_{LA} and ω_{LB} measured for ^{111}Cd , which most probably [51] substitutes the two cation sites A (tetrahedral; Fe^{3+}) and B (octahedral; charge exchange between Fe^{2+} and Fe^{3+}) in magnetite (= ferrimagnetic Fe_3O_4) [46]. It is interesting to note that the two values of $\beta_A = \beta_B = 0.392(2)$ are in perfect agreement with each other and very close to the ones expected for a Heisenberg magnet. While the A-site oxygen surrounding is cubic ($\nu_{QA} = 0$), the B-site features a finite, symmetric EFG, $\nu_{QB} = 42(2)$ MHz, $\eta_B = 0$, measured at $T = 873$ K, well above $T_N = 848$ K. The combined interaction at the site B below T_N leads to a line broadening in the EFG signal ($\delta_B = 20 - 25$ MHz, Fig. 3b) which is much larger than the one of the purely magnetic interaction at site A ($\delta_A = 2 - 5$ MHz).

The temperature dependence of the magnetic hyperfine fields on the A and B sites in magnetite has been measured very carefully by means of ^{57}Fe -Mössbauer spectroscopy (MS) [52], while the sublattice magnetizations have been determined by neutron diffraction [53]. As discussed in detail by de Grave et al. [52], good agreement was found among the results of the two methods, but significant deviations from the 3D Heisenberg model! In the equation

$$\omega_{Li}(T)/\omega_{Li}(0) = \langle S_{zi}(T) \rangle / S_i, i = A, B,$$

the quantity $\langle S_{zi}(T) \rangle$ is the expectation value of the z -component of the ionic spin S_i at temperature T . It can be expressed as

$$\langle S_{zi}(T) \rangle = \frac{B_{si}}{kT} \{ 2z_{ii}J_{ii}\langle S_{zi}(T) \rangle - 2z_{ij}J_{ij}\langle S_{zj}(T) \rangle \},$$

where B_{si} denotes the so-called Brillouin function at site i , z_{ij} is the number of magnetic cations of type j in the nearest-neighbor shell of cation i and J_{ij} the corresponding superexchange integral along the path $\text{Fe}_i\text{--O}^{2-}\text{--Fe}_j$. The calculated exchange integrals are $J_{AA} = -11$ K and $J_{AB} = J_{BA} = -22$ K. The value of J_{AB} is typical of the $\text{Fe}_A^{3+}\text{--O}^{2-}\text{--Fe}_B^{3+}$ chain and thus indicates *ferrimagnetic* ordering for the AA and AB pairs. The small positive value of $J_{BB} = +3$ K indicates *ferromagnetic* behavior for the BB pairs. These findings imply the validity of a conventional molecular-field approach of localized spins at the A site, but need to account for the non-localized sixth 3d electron of the Fe^{2+} ion at the B site. Calculations with the non-localized electron model by Kubo and Ohata [54] have successfully reproduced the hyperfine field at the B site. The subtle difference between the MS and PAC data appears to be a consequence of the fact that no charge fluctuations occur for the ^{111}Cd probe, leading to an interpretation of both sites with localized electrons. This difference therefore is a first

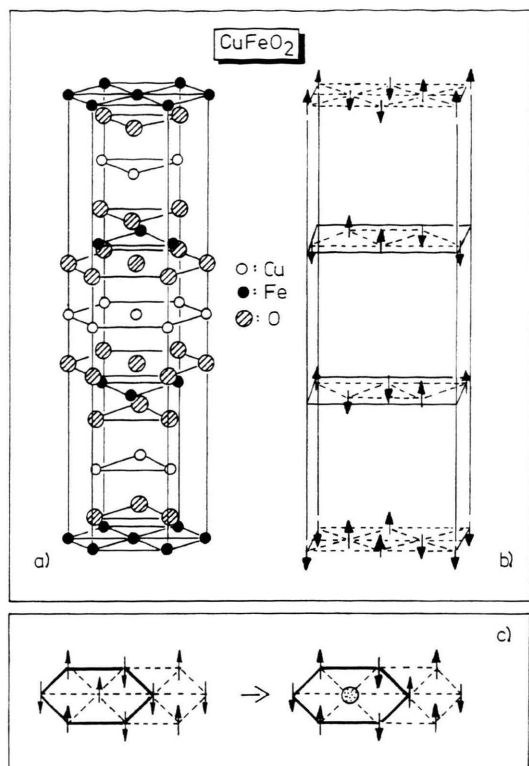


Fig. 4. Crystal structure of the CuFeO_3 delafossite. The spin frustration within the 2D triangular Fe sublattice (left) is removed by substitutional $^{111}\text{In}/^{111}\text{Cd}$ impurity atoms (right). From [22].

indication that the impurity probe atom introduces a significant change into the system.

Another interesting phase transition of Verwey type in magnetite was studied with PAC [51]: This transition around 125 K is also visible in Fig. 3a as a sudden increase of ω_{LA} from 178 MHz at 140 K to 191 MHz at 100 K. In the same temperature interval, the Larmor frequency ω_{LB} drops from 173 MHz to 151 MHz (see Fig. 3a), while both δ_{A} and δ_{B} strongly increase below T_{V} (Figure 3b). The dramatic changes of the Larmor frequencies $\omega_{\text{LA,B}}$ and distribution widths $\delta_{\text{A,B}}$ at the Verwey transition have been correlated with either the presence of several hyperfine environments below T_{V} which were also seen in Mössbauer spectroscopy [52, 55, 56], the structural phase transition from cubic to monoclinic structure, and/or electronic after-effects (due to the change of the conductivity at T_{V} from conductor to insulator).

So far, the role of the dilute $^{111}\text{In}/^{111}\text{Cd}$ probe atoms was that of more or less ideal “spectators” monitoring

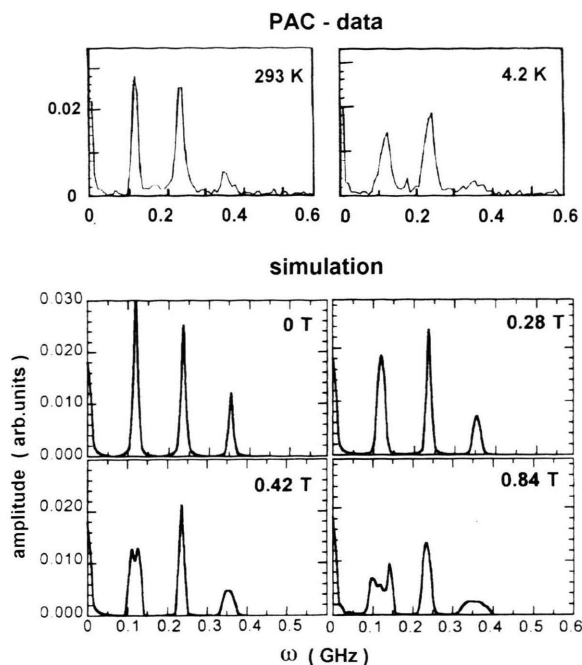


Fig. 5. Measured and calculated Fourier transforms of combined electric and magnetic hyperfine interactions in CuFeO_3 in the limit of a small magnetic hyperfine field [22]. T means Tesla.

the magnetic ordering of the matrix without influencing it. A contrasting behavior was found in the case of polycrystalline CuFeO_2 , where the probes on particular lattice sites determine the spin ordering [22]. The crystal structure of the $\text{A}^{1+}\text{B}^{3+}\text{O}^{2-}_2$ delafossite CuFeO_2 , Fig. 4, can be seen as a sequence of monoatomic layers, all with triangular structure. The magnetically ordering Fe layers are separated from each other by two oxygen layers and a Cu layer. This leads to a 2D spin-frustrated AF within the triangular Fe sublattice. When the magnetic hyperfine field below the Néel temperatures $T_{\text{N}} = 11$ K and 16 K was measured via ^{57}Fe -Mössbauer spectroscopy, a hyperfine field of normal size, $B_{\text{hf}} = 51.7$ T, was identified at 4.2 K for the Fe site, besides the occurrence of a large EFG [57]. On the other hand, when the hyperfine field was measured via ^{111}In -PAC, the resulting value of $B_{\text{hf}} = 0.3(1)$ T was found to be much smaller. This low value of B_{hf} was explained by the regular antiparallel spin ordering of the six immediate Fe neighbors around the ^{111}Cd probe whose hyperfine fields should cancel each other, because now the spin frustration is relieved (see Figure 4). The Fourier spectra of the perturbation functions measured below T_{N} ($T_{\text{m}} = 4.2$ K)

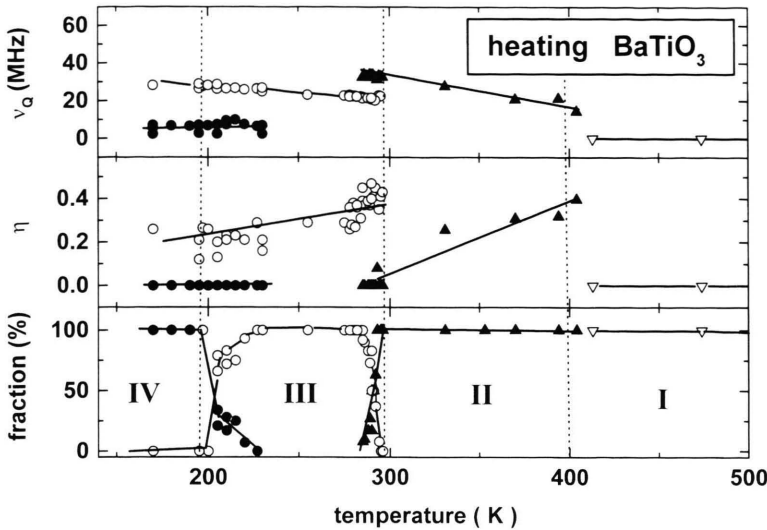


Fig. 6. Temperature variation of the ^{111}Cd electric quadrupole interaction parameters ν_Q , η and the fraction of different EFGs for BaTiO_3 . Dashed lines mark the phase transitions according to the literature.

show a broadening and reduction in height of the first EFG harmonics ω_1 , relative to that measured above T_N ($T_m = 293$ K). The simulated Fourier spectra shown in Fig. 5 confirm the small value of B_{hf} . The interpretation rests on the assumption that ^{111}In occupies the B^{3+} (Fe) sites. Support for this interpretation came firstly from the magnitude and asymmetry of the EFG and secondly from PAC experiments with ^{111}Ag probe atoms which, of course, occupy the A^{1+} sites and therefore exhibit a very different EFG [36]. Both types of EFGs were also found in the PAC data obtained with ^{111}Ag or ^{111}In probes in the delafossite AgInO_2 where the probes are self-atoms.

4. Structural Phase Transitions

While magnetic phase transitions only involve changes of spin directions, we now proceed to the discussion of phase transitions, due to changes in the atomic positions, but still not in the composition of the compounds. Perovskite oxides of the structure $\text{A}^{2+}\text{B}^{4+}\text{O}_3^{2-}$ exhibit complex structural instabilities such as ferroelectric or antiferroelectric distortions, which have been investigated extensively [58]. A perfect perovskite crystal has full cubic symmetry and can be imagined as a lattice of corner-sharing oxygen octahedra. Cation B – the smaller one – is located in the center of an oxygen octahedron, whereas cation A is at the 12-fold coordinated site between the octahedra. Typical structural phase transitions concern either the octahedral network (tilting or twisting the octahedra towards each other), the individual shapes

Table III. Electric field gradients of ^{111}Cd and ^{181}Ta probes in BaTiO_3 , at the given temperatures [39].

Probe nucleus Phase	^{111}Cd			^{181}Ta [4 - 6]		
	T (K)	ν_Q (MHz)	η	T (K)	ν_Q (MHz)	η
IV, rhomboh.	80	6.3(24)	0	80	63(17)	0
III, orthorh.	227	22.0(8)	0.37(6)	220	137(12)	0.4(1)
II, tetragonal	293	33.3(7)	0	293	205(12)	0
I, cubic	475	0	0	400	0	0

of the octahedra (deformations along the axes) or the location of the cations, which may be shifted out of their central positions.

We have performed PAC measurements with implanted ^{111}In probes to study structural phase transitions in BaTiO_3 , SrTiO_3 , BaHfO_3 , SrHfO_3 and PbZrO_3 perovskites [37 - 39]. When the temperature is raised from 150 to 400 K, BaTiO_3 – of highest interest due to its piezoelectric properties [59] – undergoes three well known phase transitions: rhombohedral (IV) \rightarrow orthorhombic (III) \rightarrow tetragonal (II) \rightarrow cubic (I). The changes between the phases involve tiny shifts of the Ti-positions in the order of only 6 pm, together with slight distortions of the oxygen octahedron [60]. Figure 6 compiles the EFG parameters ν_Q and η of the different phases during heating sequences. Each phase is characterized by a single EFG (with a fraction of 100%), different in strength and symmetry. The PAC parameters are listed in Table III. The ferroelectric transitions IV \rightarrow III and III \rightarrow II are structural phase transitions of first order with a discontinuous change of the order parameter. As a consequence a certain temperature range exists where both

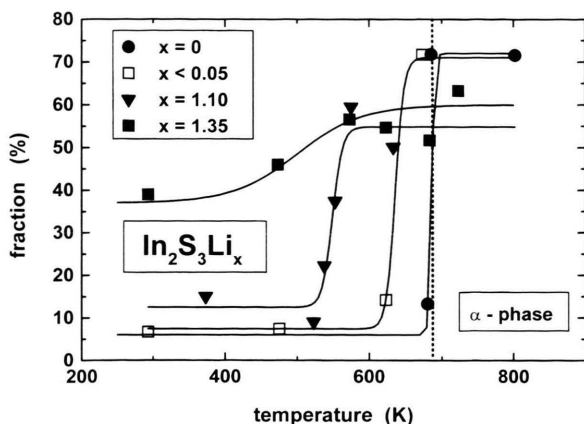


Fig. 7. Temperature dependence of the occurrence of an α -phase like fraction in β - In_2S_3 samples which have been doped with different amounts x of Li-atoms.

phases coexist, giving rise to an hysteresis. If we define the transition temperature T_0 by requiring that both fractions reach 50%, the hysteresis leads to two transition temperatures $T_0^{\uparrow/\downarrow}$ for heating and cooling cycles, separated by the interval $\Delta T = |T_0^{\uparrow} - T_0^{\downarrow}|$. As shown in detail in [40], in the case of BaTiO_3 we found $\Delta T = 7.5$ K for the $\text{IV} \rightarrow \text{III}$ transition and $\Delta T = 6.1$ K for the $\text{III} \rightarrow \text{II}$ transition. Compared to other methods there are slight differences in the values of ΔT and also in T_0 , but PAC surely is the most local indicator of the hysteresis [40]. The temperature dependence of the parameters ν_Q and η in each phase shown in Fig. 6 can easily be explained by the thermal changes of the lattice constants in these phases, as will be shown below.

Another type of structural phase transitions related to changes in the next-neighbor polyhedra occurs in the spinel In_2S_3 . In the β -phase the self-atom ^{111}In occupies all possible cation sites of the sulphur-polyhedra, according to the probabilities imposed by the crystallographic order. These are two octahedral sites \mathcal{O}_1 and \mathcal{O}_2 of somewhat different geometry and one tetrahedral site \mathcal{T} . Nevertheless, one third of all existing coordination tetrahedra is not occupied by In-ions, in a fixed crystallographic order. The phase transition to the cubic α -phase occurs at $T = 693$ K and results in a random order of the non-occupied tetrahedra. In fact, the PAC spectra show a dynamical behaviour (see Sect. 5) which is attributed to In-ions jumping between empty S-tetrahedra, within the PAC observation time [62]. A high amount x of Li-atoms can be intercalated into the spinel structure (on non-regular

lattice sites) to form β - $\text{In}_2\text{S}_3\text{Li}_x$. As shown in Fig. 7, a dramatic reduction of the phase transition temperature occurs for increasing Li content x . The observed PAC parameters are equal to those, found in the Li-free α -phase. Therefore, one has to assume that the electrically active Li-atoms lower the binding of the In-ions inside a sulphur tetrahedra: now the In-ions jump between empty tetrahedra which results in the random distribution of the α -phase.

Excursion to the Calculation of EFGs in Oxides

In many oxides, PAC measurements have been carried out with the standard probes $^{111}\text{In}/^{111}\text{Cd}$ and $^{181}\text{Hf}/^{181}\text{Ta}$. For the quadrupole frequencies ν_Q associated with substitutional, defect-free sites, their ratio was in general found in agreement with the value $\nu_Q(^{181}\text{Ta})/\nu_Q(^{111}\text{Cd}) = 6.5 \pm 1.0$ predicted by the Point Charge Model (PCM). In addition, agreement was found for the experimental asymmetry parameters η . In the following, we shortly discuss some of the successes and failures of PCM and the possibility to identify lattice locations and refine atomic positions. This, of course, directly bears on the possibility of following structural phase transitions.

EFGs can be calculated *ab initio*, even in complex compounds [63], if an appropriate band structure description of that compound is available. Whenever the bonding of oxides can be supposed to be mainly ionic, a simple PCM may be applied to calculate the EFG for probes at cation sites, as was shown by Frantz et al. from a comparison of PCM with a Hartree-Fock and a LAPW calculation [64]. Assuming formal point charges for the anions and cations at their crystallographic locations, the lattice sum V_{ij}^{lat} can be calculated [7, 28]. As to the problem of convergence of the lattice sum in the case of the r^{-3} dependence of the EFG and the r^3 dependence of the integration volume, convergence was found in all cases when a cut-off radius of 5 nm around the probe ion was used [7]. Writing the EFG tensor at the probe nucleus as $V_{ij} = (1 - \gamma_\infty)V_{ij}^{\text{lat}}$ and using the known Sternheimer antishielding factors $\gamma_\infty(^{111}\text{Cd}) = -29.27$ and $\gamma_\infty(^{181}\text{Ta}) = -68.12$ [65] and quadrupole moments $Q(^{111}\text{Cd}) = 0.83(13)$ b and $Q(^{181}\text{Ta}) = 2.36(5)$ b [4], respectively, one finds the ratio $\nu_Q(\text{Ta})/\nu_Q(\text{Cd}) = 6.5(10)$ [37]. Table IV summarizes EFG parameters of several perovskites and of monoclinic HfO_2 and ZrO_2 and indeed demonstrates the usefulness of the PCM to identify substitutional sites in these oxides.

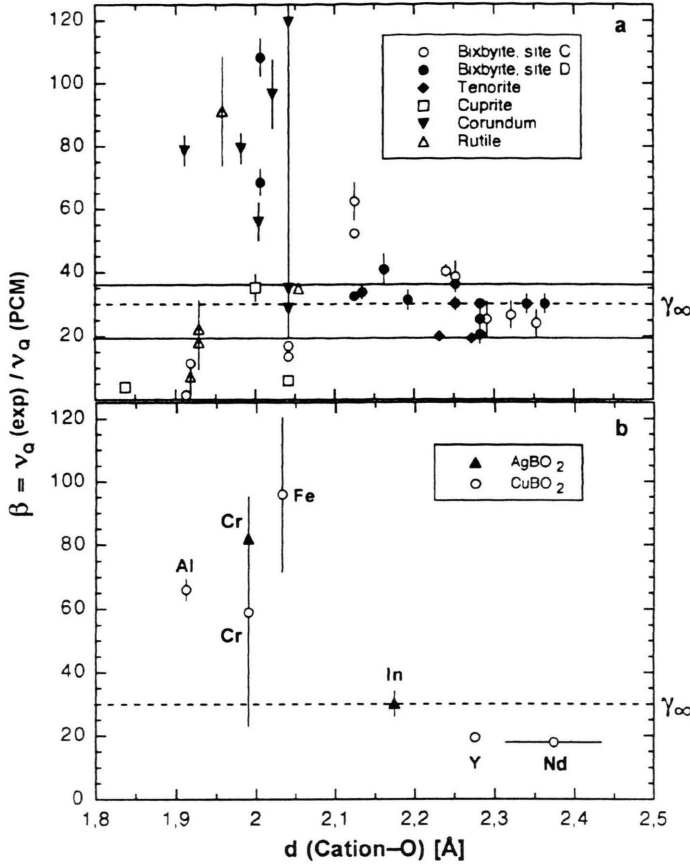


Fig. 8. The ratio $\beta = \nu_Q(\text{exp}) / \nu_Q(\text{PCM})$ is plotted versus the bond length d (cation-O) in oxides (a) taken from the compilation in [7] and (b) from the delafossite data of [35, 36].

Table IV. Comparison of the quadrupole interaction with ¹⁸¹Ta and ¹¹¹Cd probes in non-cubic compounds [38].

Comp.	Struct.	¹⁸¹ Hf/ ¹⁸¹ Ta		¹¹¹ In/ ¹¹¹ Cd		$\frac{\nu_Q(\text{Ta})}{\nu_Q(\text{Cd})}$
		ν_Q (MHz)	η	ν_Q (MHz)	η	
SrHfO ₃	orthorh.	130(4)	0.45(6)	21.6(13)	0.51(6)	6.0 (3)
PbZrO ₃	orthorh.	522(6)	0.84	93(5)	≈ 1	5.6 (3)
BaTiO ₃	tetrag.	205(5)	0.15(5)	31.2(30)	0.25(6) ^a	6.6 (8)
HfO ₂	monocl.	783(6)	0.34(3)	111(2)	0.60(3)	7.1 (2)
ZrO ₂	monocl.	719(6)	0.33	111(2)	0.64(4)	6.5 (2)
PCM						6.5(12)

^a mean value over the whole range of phase existence.

More important in the context of structural phase transitions was the systematic investigation of the r^{-3} dependence of the EFG. We used classes of oxides having the same crystalline structure, but different lattice constants. In this way, the cation bond lengths were varied in a controlled way. Extensive studies were done in the bixbyites ($\text{A}^{3+}_2\text{O}^{2-}_3$), among them the only stable indium oxide In_2O_3 [30, 66, 67]. A second class for such studies were the

cuprates $\text{M}_2\text{Cu}_2\text{O}_5$ [34] and finally the delafossites $\text{A}^{1+}\text{B}^{3+}\text{O}^{2-}_2$ which span the widest range of lattice parameters [35]. In all three classes a smooth dependence of the EFG parameters ν_Q and η on the average bond length $\langle d \rangle^{-3}$ was found. An appropriate way to illustrate the result of this comparison is plotting the ratio $\beta(\text{exp}) = \nu_Q(\text{exp}) / \nu_Q(\text{PCM})$ versus the bond length $\langle d \rangle$ averaged over all next-neighbor oxygen ions (see Fig. 8 [35]). Most data with $\langle d \rangle \geq 2.1$ Å are found within the range $19 \leq \beta(\text{exp}) \leq 36$. The weighted experimental average is $\beta \geq 32(2)$ which is in good agreement with the calculated value $\beta_\infty = (1 - \gamma_\infty(^{111}\text{Cd})) = 30.3$, given as the dotted line. For smaller bond lengths, the data seem to split into two branches, one with the high value of $\beta \approx 85$ and the other one with values below $\beta \approx 10$. The critical distance of 2.1 Å has a simple interpretation: it is the sum of the Shannon radii [68] of O^{2-} and Cd^{2+} ions. A shorter distance is equivalent to an overlap of the electronic shells, giving rise to covalent bonding and additional contributions to the EFG, possibly with dif-

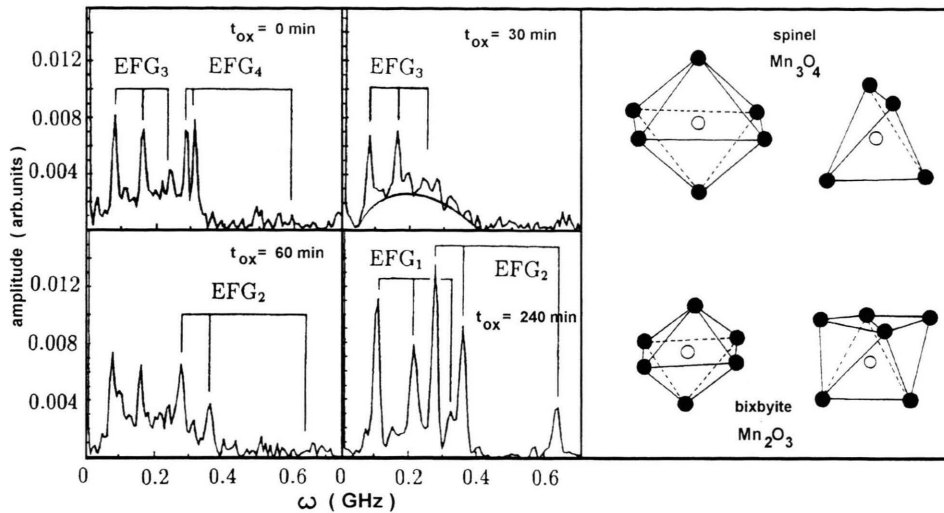


Fig. 9. Fourier transforms of PAC spectra taken at 480 K and $p \leq 10^{-5}$ mbar after oxidizing Mn_3O_4 at 770 K for different times t_{ox} . On the right hand side the different oxygen-polyhedra and their transformations are indicated [48, 9].

ferent signs. The delafossite data displayed in Fig. 8b gave more insight into the questions, whether β depends on the crystalline structure or on the bond length or whether it clusters within certain regions of bond lengths. The delafossite data extend over the whole range of $\langle d \rangle$ covered by the binary oxides shown in Fig. 8a and feature a smooth dependence [35, 36].

Finally, we shall discuss the accuracy in determining crystalline coordinates in the class of bixbyite oxides by means of PAC. The determination of atomic positions of the light elements in compounds made from atoms of very different element number Z by X-ray diffraction is complicated. In oxides containing very heavy metal components, one usually relies on neutron diffraction. Realizing the pronounced scatter of calculated EFG parameters in the bixbyite oxides when using the published structure data in the PCM calculations, Bartos et al. [28] in turn used the precisely measured quadrupole interaction parameters to refine the atomic positions to a precision of better than 1 pm and still found agreement with the less precise coordinates obtained from X-ray and neutron diffraction [28]. The new bond lengths vary smoothly with the lattice constants. As an additional test, Lupascu et al. [30] performed precision PAC measurements in Er_2O_3 and Ho_2O_3 single crystals and achieved a refinement at the level $1 \cdot 10^{-4}$. The coordinates obtained in this way agreed with the high-precision X-ray diffraction data taken for the same crystals.

Having in mind this high sensitivity of PAC to small variations of atomic coordinates, Krishnamurthy et al. [69] studied the spin-Peierls phase transition in CuGeO_3 using ^{111}In -PAC. Below the critical temperature of $T_{\text{SP}} = 14$ K, adjacent Cu^{2+} ions undergo spin dimerization and form $\text{Cu}^{2+} - \text{Cu}^{2+}$ pairs along the c -axis, verified by different techniques as X-ray diffraction, electron- and neutron diffraction (see Ref. in [69]). When these Cu-dimers are built, the distance between the dimers is slightly larger than the distance within the pair. This shift is accompanied by alternating inward and outward displacements of the two O^{2-} ions in the Cu-O-Cu chains along the c -axis. These positional changes at the structural phase transition might change the asymmetry parameter η and/or the EFG. However, no effect was observed: either these positional changes are too small to be detected, or we find again the influence of the impurity probe atom. The In atom cannot build a dimer with Cu and locally destroys the spin-Peierls transition.

5. REDOX Phase Transitions in Oxides

Phase diagrams of metals and oxygen often show the existence of several stable oxide phases with different stoichiometries. Consequently, many metals in contact with air build oxide surface layers, sometimes sequences of layers with different oxide stoichiometries. Problems of corrosion, atomic transport during

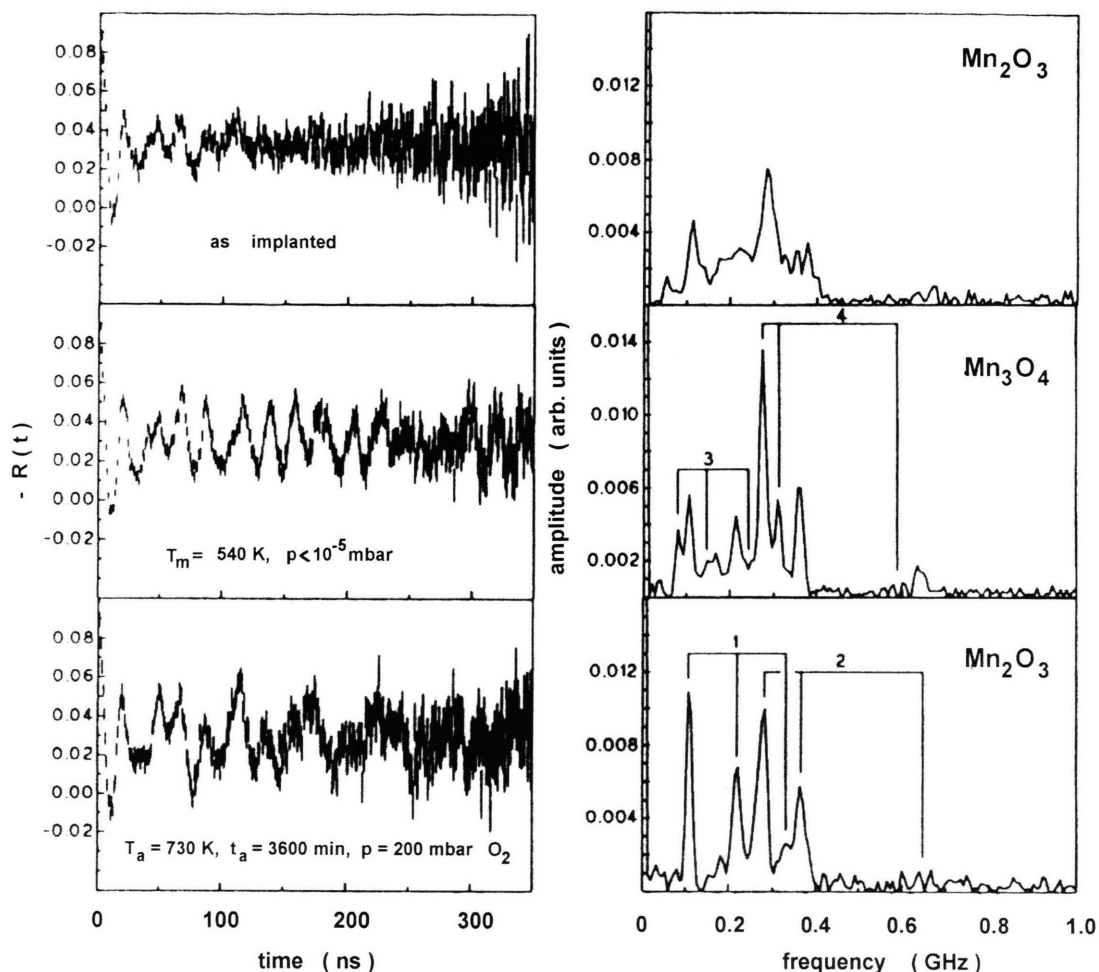


Fig. 10. PAC spectra of a complete REDOX phase transition cycle. After the implantation of ^{111}In into Mn_2O_3 (top) this oxide was reduced to Mn_3O_4 at 540 K in high vacuum and measured under these conditions (middle). An oxidation at 730 K for 60 h restored Mn_2O_3 . This spectrum was taken at room temperature [48, 73].

oxidation and/or the occurrence of defects call for a microscopic observation of oxidation and reduction reactions. Such REDOX phase transitions dramatically change the crystalline structure, i. e. the oxygen polyhedra and/or the charge state(s) of the cation(s). In general, all these phenomena can be observed by the PAC technique. However, when realizing such REDOX phase transitions experimentally, a kind of asymmetry occurs: heating metals or lower oxides in oxygen easily increases the oxygen content of the sample. On the other hand, annealing treatments of an oxide under a standard vacuum is – in most cases – not enough to achieve a reduction. As an example, the rutile TiO_2 can only be reduced to Ti_3O_5 via an

increasing oxygen deficit under the very low oxygen partial pressure of 10^{-9} hPa at 1600 K [70, 71]. Therefore, a thermal treatment below 1600 K under a pumped vacuum of 10^{-5} hPa does not reduce any Ti-oxide. Experimentally such a low oxygen activity can be realized by using a controlled gas mixture of CO and CO_2 , as was applied in the PAC studies on CoO, NiO and Cr_2O_3 [50, 72, 25, 31].

As an example, we present results on the REDOX phase transition in manganese oxides obtained by Wiarda and collaborators [48]. The phase transition between the spinel Mn_3O_4 and the bixbyite Mn_2O_3 can be driven in both directions without big experimental difficulties. Figure 9 illustrates the *oxidation*

of Mn_3O_4 to Mn_2O_3 at 770 K in 200 mbar O_2 for increasing oxidation times t_{ox} . The evolution of the oxidation process was followed by accumulating the PAC spectra at $T_m = 480$ K in high vacuum [48]. Each of the two crystal structures contains two non-equivalent cation sites represented at the right hand side of Fig. 9 by their characteristic oxygen polyhedra. Surprisingly, the phase conversion seems to proceed stepwise and with different velocities for the different polyhedra. First the signal EFG_4 from ^{111}In -ions occupying tetrahedral sites in Mn_3O_4 (four next neighbors at 2.63 Å) converts into a broad distribution, while the octahedral site (two NN at 2.29 Å and four at 2.63 Å, symmetric EFG_3) remains stable. The octahedron in Mn_3O_4 is still dominantly present (EFG_3) when a large amount of probes already feels the asymmetric octahedron of Mn_2O_3 (6 NN at 2.04 Å, EFG_2). In this state, the structure of the sample is neither a spinel nor a bixbyite! Finally, the environments of the remaining probes reorder to form the symmetric octahedra (six NN at 2.003 Å) giving rise to EFG_1 . X-ray diffraction before and after the phase transition showed a complete transformation of the full polycrystalline sample. It should be mentioned here that Mn_3O_4 is one of the very rare cases where the ^{111}In probes are found at the center of an oxygen tetrahedron. In fact, during the oxidation process, this site disappears first. On the other hand, the right hand side of Fig. 9 suggests, that the tetrahedron can easily be transformed into the irregular octahedron by attracting two more oxygen ions in an upper plane.

Figure 10 shows PAC data accumulated during the *reduction* reaction of the same Mn-oxides [73]. ^{111}In was implanted into Mn_2O_3 . Due to radiation damage the oscillations in the PAC spectra are damped in the as-implanted spectrum. The second spectrum measured at $T_m = 540$ K under high vacuum conditions exhibits the EFGs typical of Mn_3O_4 . The subsequent oxidation at 730 K with 200 mbar O_2 for 60 hours leads back to a well defined Mn_2O_3 spectrum, measured at room temperature. Figure 10 thus illustrates a complete cyclic REDOX phase transition and proves that this kind of phase transition efficiently anneals out radiation damage: after this rearrangement of the whole sample, large fractions of the implanted ^{111}In probes sit on well-defined substitutional sites.

From a chemical point of view REDOX phase transitions change the charge state of ions in the compound. In oxides the O ions usually stay in the charge state -2 , while the charge state(s) of the cations

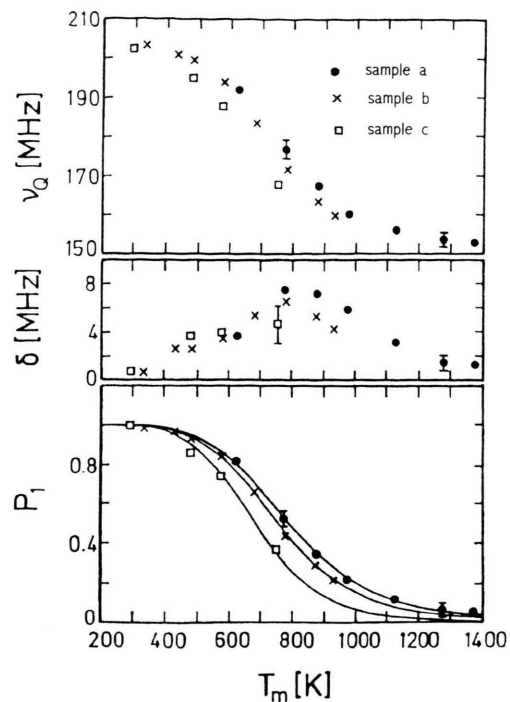


Fig. 11. Temperature dependent coupling constant ν_Q (top), distribution width δ (middle) and equilibrium probability P_1 in Cr_2O_3 [31]. P_1 represents the probability to observe EFG_1 in the two-state model of [12]. The data refer to three samples (a-c) implanted with different ^{111}In -doses and then annealed at 1370 K in air.

change. In the bixbyite Mn_2O_3 all Mn ions have the charge $+3$, but in the normal spinel Mn_3O_4 one third of the Mn ions have a charge of $+2$, the rest remaining at $+3$. Such changes occurring in the immediate neighborhood of the hyperfine probe will strongly affect the strength(s) of the EFG.

Even faster changes of the ion charges, possibly occurring many times within the observation time (≈ 200 ns) of the hyperfine-sensitive probe, may be due to charge fluctuations, as already discussed in the case of magnetite (see Section 3). Such rapid changes will necessarily influence the PAC spectra and may introduce a dynamic hyperfine interaction. Neubauer et al. [30] found such charge fluctuations to occur in the wide-gap semiconductor Cr_2O_3 . As it has corundum structure, like Al_2O_3 [33] and Rh_2O_3 [74], one expects a single equivalent cation site with axial symmetry ($\eta = 0$). However, after a moderate annealing at 973 K, the experiments revealed *two* well defined EFGs, having the parameters $\nu_{Q1} = 202(1)$ MHz, $\eta_1 = 0$ and $\nu_{Q2} = 151(1)$ MHz, $\eta_2 = 0$. Both EFG tensors have

the largest component V_{zz} pointing along the [111] axis of the rhombohedral unit cell as expected for probes on substitutional sites. A longer annealing at 1370 K resulted in the observation of a single EFG having the average quadrupole frequency $\langle\nu_Q\rangle$. It varied between the limits ν_{Q2} and ν_{Q1} and was reversible as function of the temperature (see the upper part of Figure 11). Strong variations of $\langle\nu_Q\rangle$ coincided with large values of the frequency width δ describing the damping of the perturbation function (see middle part of Figure 11).

In the semiconductor Cr_2O_3 the dominant defect charge carriers in thermal equilibrium are electron holes [75]. If one assumes the trapping and release of holes at the Cr^{3+} ion next to a substitutional ^{111}In probe, all phenomena in the PAC experiment can be fully explained by the dynamical two-state model of Achtziger and Witthuhn [12]. The jump rates κ_2 (trapping, $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$) and κ_1 (release, $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$) sensitively depend on the overall defect concentration, and the ratio of these two rates directly determines the average frequency $\langle\nu_Q\rangle$ and damping δ of the PAC spectra [12]. Minor changes in the impurity concentrations already cause different transition temperatures from the defect-trapped to the defect-free configuration, as shown in Fig. 11 for differently implanted samples a - c. This microscopic picture of a charge fluctuation of a neighboring Cr-ion could be backed by PCM calculations. Introducing a small relaxation of 0.29 Å for the oversized ^{111}In probe away from the Cr-neighbor we are able to reproduce *both* EFGs in their direction *and* strengths [31, 8]. The lower part of Fig. 11 gives the calculated temperature-dependence of the probability P_1 to feel EFG_1 . If these curves are interpreted in the framework of the Shockley-Read-statistics we find an activation energy of $E = 0.47(8)$ eV which agrees with the activation energy for electron hole conductivity of 0.25 - 0.6 eV (see Refs. in [31]).

It should be mentioned here that this special case of a dynamic hyperfine interaction is rarely observed, whereas other dynamic processes related to the EC-decay after-effects of ^{111}In (see for an overview [76]) occur in quite a lot of oxides. Indeed, many PAC spectra of semiconducting or isolating oxides show a strong damping in the temperature range from 100 to 300 K, which disappears reversibly at lower and higher temperatures. The reason for the non-static

hyperfine interaction(s) are slow electron transport processes in the 100 ps to 100 ns time range, due to the lack of free electrons and/or their slow diffusivity in the lattice, necessary to re-install a stable electron configuration of the ^{111}Cd daughter atom. Proof of this explanation of the damping was obtained by control experiments with γ -decaying $^{111\text{m}}\text{Cd}$ probes, implanted into the same samples at ISOLDE/CERN. Alternatively, by doping the oxide with electron donors, the missing electrons can be provided as was shown in the case of Ce-doped La_2O_3 [16, 9, 14]. Different scenarios of dynamic processes have been developed by Lupascu and collaborators [9,14] and also applied in the case of La_2O_3 [16] and In_2O_3 [15].

6. Conclusions

This survey has demonstrated that oxides offer a wide range of phase transitions to be studied with PAC. The $^{111}\text{In}/^{111}\text{Cd}$ impurity hyperfine probes in many cases can be positioned onto substitutional defect-free sites and can monitor magnetic, structural or chemical changes occurring in their immediate neighborhood. However, we have also indicated limitations of the technique, due to the different chemical nature of the mother (In) or daughter (Cd) impurity and the radioactive decay of ^{111}In to ^{111}Cd .

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