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A Perturbed-Angular-Correlation Study of Hyperfine Interactions at ^{181}Ta in α-Fe_2O_3

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Abstract. The hyperfine interactions at ^{181}Ta ions on Fe^{3+} sites in α-Fe_2O_3 (hematite) were studied in the temperature range 11–1100 K by means of the perturbed angular correlation (PAC) technique. The ^{181}Hf(β^-)^{181}Ta probe nuclei were introduced chemically into the sample during the preparation. The hyperfine interaction measurements allow to observe the magnetic phase transition and to characterize the supertransferred hyperfine magnetic field B_{hf} and the electric field gradient (EFG) at the impurity sites. The angles between B_{hf} and the principal axes of the EFG were determined. The Morin transition was also observed. The results are compared with those of similar experiments carried out using ^{111}Cd probe.

Key Words: electric field gradient, hematite, perturbed angular correlation, supertransferred magnetic field.

1. Introduction

The magnetic hyperfine fields in iron oxides have been the subject of several investigations in the past, specially using Mössbauer spectroscopy [1]. Supertransferred hyperfine fields at ^{111}Cd impurity sites in iron oxides were measured by means of the Perturbed Angular Correlation (PAC) technique [2–7]. These studies provided valuable information on the magnetic phase transitions involved in magnetite (Fe_3O_4) and hematite (α-Fe_2O_3). An interesting feature of these experiments is that while aftereffects of the EC decay of ^{111}In to ^{111}Cd appear to play a role in the second case [5–7] they are absent in the first one [2–4, 8]. The aim of the present paper is to investigate the hyperfine fields at ^{181}Ta impurity site in α-Fe_2O_3 by means of the other commonly used PAC radioactive isotope ^{181}Hf, which decays to ^{181}Ta through β^- emission. Aftereffects due to the decay should not occur because the upper level of the 133–482 keV γ–γ cascade has a half life of 12 μs, sufficiently long to allow for electronic adjustment prior to coincidence counting.

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Among the iron oxides, corundum-type α-Fe_2O_3 (hematite) is the most common on earth. At room temperature, it crystallizes in the rhombohedral corundum structure (space group $R\bar{3}c$). The magnetic moments of Fe^{+3} ions are ordered antiferromagnetically below the Néel temperature T_N = 955 K. As the $^{181}Hf \rightarrow {}^{181}Ta$ probe is expected to substitute the Fe^{+3} in the α-Fe_2O_3 lattice and since the point symmetry of these sites is trigonal with a three-fold axis parallel to [111] axis, ^{181}Ta should experience an axially symmetric Electric Field Gradient (EFG) along this direction. Below the Neél temperature, α-Fe_2O_3 is an antiferromagnetic insulator showing weak ferromagnetism above the Morin temperature, T_M = 260 K due to a slight canting of the two sublattice magnetizations. Below T_M, the direction of the magnetic moments is parallel to the [111]-axis of the hexagonal unit cell while above T_M, the magnetic moments lie in the (111) plane.

2. Experimental

Polycrystalline samples of Fe_2O_3 doped with ^{181}Hf were prepared by adding $\sim$100 μCi of ^{181}Hf as HfF_4 in a dilute hydrofluoric acid solution to a solution of $Fe(NO_3)_3$ obtained by dissolving iron metal in concentrated HNO_3. The radioactive ^{181}Hf was obtained by irradiating approximately 1 mg of Hf metal in the IEA-R1 reactor at IPEN for 64 h with a neutron flux of $\sim 2 \times 10^{13}$ n/cm^2.s. The solution was evaporated to complete dryness and the resulting powder was pressed into a small pellet and sintered for 12 h at 1100 K in air. The PAC spectra were recorded at several temperatures, between 11–1100 K, using a standard setup with four conical BaF_2 detectors arranged in a planar 90–180° geometry, generating simultaneously 12 delayed coincidence spectra. The detector system had a time resolution of $\sim$600 ps. A small tubular furnace was used for the measurements above room temperature and the temperature was controlled to within 1 K. For low-temperature measurements the sample was attached to the cold finger of a closed-cycle helium refrigerator with temperature controlled to better than 0.1 K. An X-ray powder diffractogramme of the sample to make sure that it is α-Fe_2O_3 would have been desirable. But it is known that the calcination of iron salts at high temperature under oxygen always produces hematite. Additionally, the quadrupole interaction data obtained in the paramagnetic phase and the determined phase transition temperature described below are unambiguous proof that we are dealing with hematite.

3. Results and discussion

Typical PAC spectra taken at some of the temperatures are shown in Figure 1. At temperatures above 955 K the spectra are well fitted assuming only one well defined electric quadrupole interaction implying that all the ^{181}Hf probes are located on the Fe^{+3} sites in the oxide and are in the identical environment. The

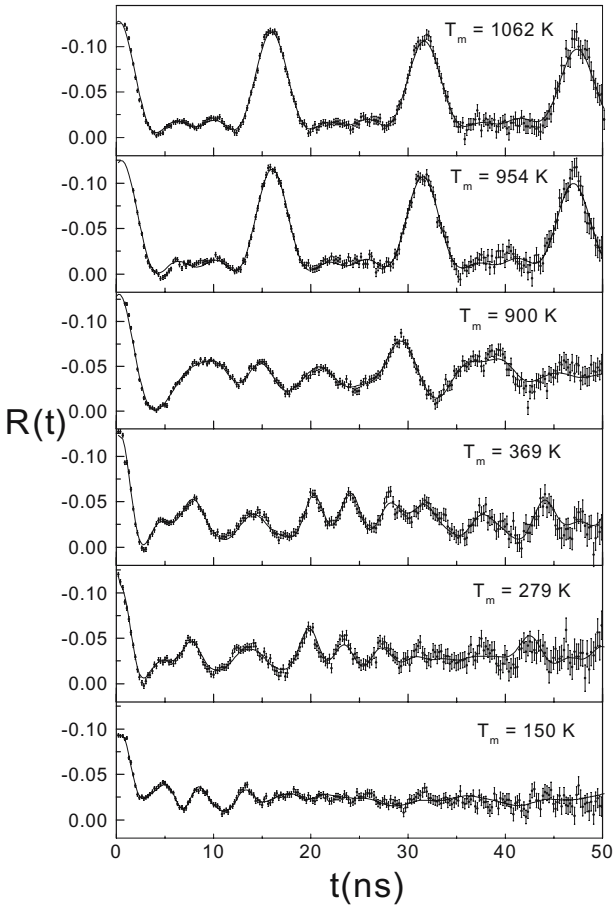

Figure 1. The PAC spectra of ^{181}Ta in α-Fe_2O_3 at different temperatures.

spectrum at 1062 K is a typical one for an axially symmetric EFG as is expected from the fact that α-Fe_2O_3 is paramagnetic at this temperature. The measured hyperfine parameters for the quadrupole interactions at temperatures $T > 955$ K remain nearly constant. The values obtained at 1062 K are: ν_Q = 424.1(4) Mhz, η = 0.06 (1) and δ = 0.016(2). Below T_N, the spectra become complex and temperature dependent indicating combined electric quadrupole and magnetic dipole interactions. The parameters of the electric field gradient show little change. The values of B_{hf} extracted from the Larmor frequency are shown in Figure 2 as a function of temperature. Just below T_N, in the critical region, we used the first eight points to fit the experimental ω_L values to the well-known power-law $\omega_L(T) = \omega_L(0)(1 - T/T_N)^{\beta}$ for magnetic materials. The resulting parameters are $\omega_L(0)$ = 842(34) Mrads/s, B_{hf} = 13.3(5) T, exponent β = 0.42(3), and T_N = 947(2) K. The value of Néel Temperature obtained here (947 K) is somewhat lower than reported earlier (955 K). Above Morin transition temperature (T_M), the angle β between the magnetic field and the Z-axis of the EFG tensor remains close to 90° in agreement with the expected value.

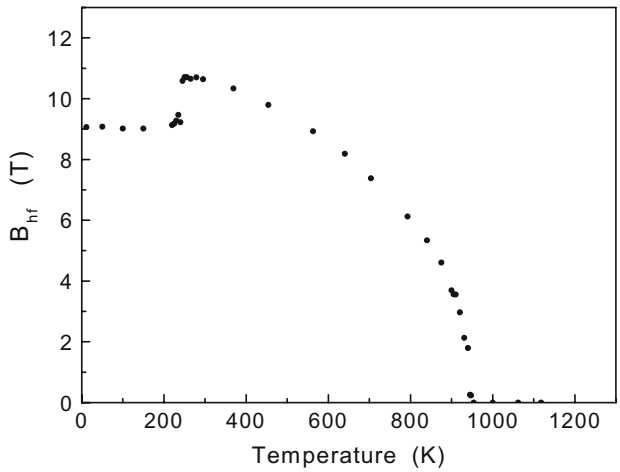

Figure 2. Values of the hyperfine magnetic field as a function of temperature.

Table I. Hyperfine parameters corresponding to the spectra of Figure 1

T_m (K)	B_{hf} (T)	ν_Q (MHz)	η	δ (%)	β (°)
1062	0	424(1)	0.06	0.02	–
954	0	430(1)	0.06	0.02	–
900	3.7(1)	433(1)	0.02	0.03	90
369	10.3(1)	437(4)	0.01	0.03	87
279	10.7(1)	442(7)	0.02	0.03	85
150	9.1(1)	431(7)	0.04	0.11	6

At T_M, the PAC spectra change dramatically, as can be seen in the spectrum at 150 K of Figure 1. Below T_M an additional combined interaction is necessary in order to obtain a good fit. This interaction involves a reduced fraction of probes (~20%). In this contribution we focus our attention in the majority component. The magnetic field shows a discontinuity in which the B_{hf} suddenly drops at around 250 K from a value of 10.7 T to 9.2 T and remains at this value till the lowest temperature. Similar discontinuities have also been observed in the measurement of the hyperfine fields at ^{57}Fe and ^{111}Cd-sites [7, 9]. Below T_M, the hyperfine fields at the ^{181}Ta and ^{111}Cd impurity-sites decrease compared to the values above T_M whereas the field at ^{57}Fe increases. In order to explain the reduced values of the supertransferred hyperfine field below T_M in the case of ^{111}Cd impurity at Fe^{+3} site a model was proposed by Asai et al. [7] in which it was suggested that the directions of the magnetic moments of the nearby Fe^{+3} ions deviate from [111] direction due to the impurity size mismatch when it substitutes a given Fe^{+3} ion. The quadrupole interaction parameters are less sensitive to this transition. The hyperfine parameters corresponding to the spectra of Figure 1 are given in Table I. The angle β between the magnetic hyperfine field and the z-principal axis of the EFG tensor is given. The data for temperatures below T_m correspond to the majority component.

4. Conclusions

We have measured the hyperfine interactions at ^{181}Ta impurities in α-Fe_2O_3 at different temperatures. PAC measurements were performed in the temperature range from 11 to 1060 K to determine the electric field gradient and B_{hf} at the impurity sites. A first principle calculation of EFG and B_{hf} at the ^{181}Ta impurity sites in α-Fe_2O_3 is under way. A model for explaining the discontinuity in the hyperfine field at T_M is under discussion.

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