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^{57}Fe HYPERFINE FIELD ANISOTROPY IN FERRITES AND ITS RELATION TO THE NON-UNIFORMITY OF THE IONIC SURROUNDING

H. ŠTĚPÁNKOVÁ, J. ENGLICH AND J. KOHOUT

Faculty of Mathematics and Physics, Charles University
V Holešovičkách 2, 180 00 Prague 8, Czech Republic

The hyperfine field anisotropy tensors, obtained from analysis of ^{57}Fe NMR spectra for iron sites in various magnetic oxides (barium hexaferrite, lithium spinel, magnetite and yttrium-iron garnet) were used to investigate the relation between the hf anisotropy and surrounding ionic arrangement. While a reasonable correlation has been found when the distribution of the nearest cations was considered, no correlation was obtained between the hyperfine field anisotropy and the positions of the nearest oxygen anions.

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1. Introduction

In ferrimagnetic iron oxides, the principal contribution to the hyperfine field on Fe^{3+} nuclei originates in interactions with the own electrons of the iron ion. Nevertheless, the crystal environment influences the hyperfine field remarkably by the electron transfer from oxygen ligands and by the electron supertransfer in the iron-oxygen-cation triads.

Ferrites were thoroughly studied by NMR and Mössbauer spectroscopy during the past decades, but no theoretical *ab initio* calculations of hyperfine interactions, reaching the precision of the experiments, are available till now, obviously because of the high complexity of the problem. Based on the experimental data, some semiempirical models and rules have, however, been developed: (i) the additivity of the transfer and supertransfer contributions from the individual neighbours is supposed to be valid with a reasonable accuracy [1, 2], (ii) the dependence of the supertransfer on the angle in the Fe-O-cation bond was proved [3], (iii) the pressure dependencies gave a quantitative estimate of the hyperfine field change induced by the change of distances between ions [4].

The contributions of the crystal environment to the hyperfine interaction consist of isotropic and anisotropic (i.e. dependent on the magnetization direction) parts. It is believed that the iron-iron superexchange mechanism has certain

common characteristics with the hyperfine supertransfer, because both these interactions are based on the transfer of unpaired electrons using the same path (the bond via the intervening oxygen) [5]. Superexchange is more akin to the anisotropic part of the transferred hyperfine interaction, as both depend on the transfer of the magnetic $3d$ electrons, while the isotropic part of the hyperfine interaction is connected with the s electrons. However, transfer to $4p$ states contributes also to the anisotropic part. From this point of view, the anisotropy part of hyperfine field is of particular interest, although its magnitude may be of an order smaller than the isotropic one.

The aim of this paper is to compare the hyperfine field anisotropy tensors obtained from NMR experiments in various ferrimagnetic oxides and to investigate the relation between the hyperfine anisotropy and the surrounding ionic arrangement of the resonating nuclei.

2. Results and discussion

Keeping in mind the intricacy of the problem, we focused on the ferrites with a collinear magnetic structure, and containing exclusively iron as a magnetic cation. Even after such a restriction, there remain numerous iron sites with various arrangements of oxygen and cation neighbourhood. The compounds used for our study and characteristics of the iron sites are listed in Table. In the non-substituted samples of the compounds the iron sites possess a local symmetry axis or symmetry plane. Besides these sites, also the sites with the diamagnetic substituent replacing one of neighbour iron cations were included in our study.

The local magnetic field at the iron nucleus, being a superposition of the hyperfine and the dipolar field, can be characterised by an isotropic part I and a symmetrical traceless tensor \hat{A} , describing dependence on the magnetization direction. The components of the \hat{A} matrix (as well as the I value) were determined by the analysis of ^{57}Fe NMR spectra and their dependence on the magnetization direction. The spectra were measured at 4.2 K. The only exception was the magnetite with the measurements performed at several temperatures above the Verwey transition T_V , when the crystal structure is cubic. The final parameters of the hyperfine field were then obtained by extrapolation to the liquid helium temperature.

The anisotropy tensor \hat{A}^{dip} of the dipolar field was calculated directly supposing that the electron magnetic dipoles of $5 \mu_B$ (or averaged moment of $4 \mu_B$ in the case of octahedral sites in the magnetite above T_V) are localised on the iron sites. The hyperfine field anisotropy tensor \hat{A}^{hf} was then obtained as a difference $\hat{A} - \hat{A}^{\text{dip}}$.

Arrangement of ions in the neighbourhood of the resonating nuclei was characterised by a matrix \hat{D} the components of which were calculated according to formula

$$D_{ij} = \sum_k \frac{r_i^k r_j^k}{(r^k)^5}, \quad i = x, y, z, \quad j = x, y, z, \quad (1)$$

where r^k is the radius vector of the k -th ion with respect to the site of the resonating nucleus. The \hat{D} matrices were calculated for several different sets of neighbouring

ions, namely the nearest oxygen polyhedron (marked by *O* as an index), nearest iron cations having magnetic moment antiparallel to the moment of the central iron ion (*S*), all nearest iron cations up to a distance of 0.4 nm (*F*), and all cations up to a distance of 0.4 nm (*C*).

TABLE

Iron sites in ferrites and anisotropy invariants^a. Cn. — coordination.

Ferrite	Site (sym.)	Cn.	G^{hf} ^b MHz ²	G^O nm ⁻³	G^S nm ⁻³	G^F nm ⁻³	G^C nm ⁻³	
hexaferrite	a(<i>D</i> _{3d})	6	0.97	0.52	2.86	1.64	1.64	
BaFe ₁₂ O ₁₉	b(<i>D</i> _{3h})	5	0.76	1.26	0.80	1.50	0.05	
	f ₁ (<i>C</i> _{3v})	4	0.11	0.62	0.0002	0.00	0.00	
	f ₂ (<i>C</i> _{3v})	6	0.09	0.09	0.46	1.03	0.32	
	k(<i>C</i> _s)	6	0.53 or 0.92	0.98	2.18	1.50	1.19	
garnet	a(<i>S</i> ₆)	6	0.049	4.54	2.26	2.26	0.00	
	Y ₃ Fe ₅ O ₁₂	a(<i>C</i> ₃) ^c	6	0.022	4.54	2.26	2.26	0.00
		a(<i>C</i> ₃) ^d	6	0.037	4.54	2.26	2.26	0.00
	d(<i>S</i> ₄)	4	0.013	4.26	0.25	0.96	0.09	
Y ₃ Fe _{5-x} Ga _x O ₁₂	a(<i>C</i> ₁) ^e	6	0.31	4.54	1.90	1.90	0.00	
Y _{3-x} Ca _x Fe _{5-x} Ge _x O ₁₂	a(<i>C</i> ₁) ^f	6	0.08	4.54	1.90	1.90	0.00	
spinel	c(<i>C</i> ₃)	4	0.38	0.00	0.028	0.028	0.00	
Li _{0.5} Fe _{2.5} O ₄	d(<i>C</i> ₂)	6	0.60 or 3.24	0.00	2.81	0.83	1.68	
magnetite	d(<i>D</i> _{3d})	6	0.75	0.00	2.92	1.75	1.75	
Fe ₃ O ₄	a(<i>T</i> _d)	4	0.00	0.00	0.00	0.00	0.00	

^aDefinitions of anisotropy invariants are given in the text. (⁵⁷Fe gyromagnetic ratio $\gamma = 1.377$ MHz/T.)

^bCalculated with partial use of published data [6-11].

^cFe³⁺ (a) on the *C*₃ axes at a distance of 0.535 nm replaced by Y³⁺ antisite defect. (The site symmetry is not destroyed completely.)

^dThe same case as previous at a distance of 1.07 nm.

^eThe nearest Fe³⁺ (d) replaced by Ga³⁺. (No local symmetry is left.)

^fThe nearest Fe³⁺ (d) replaced by Ge⁴⁺.

To obtain a single quantity describing the extent of the anisotropy, the value of the tensor invariant defined by the formula

$$G = [(A_{xx}^{hf} - A_{yy}^{hf})^2/3 + (A_{xy}^{hf} + A_{yx}^{hf})^2/2] + \text{cyclic} \tag{2}$$

was calculated for each \hat{A}^{hf} and analogously for \hat{D} matrices.

The results obtained are summarised in Table. Correlation between the nonuniformity of the ionic vicinity and the hyperfine field anisotropy was quantified by the value of the cross-correlation coefficient. A medium positive correlation was found between the anisotropies of the hyperfine field and the arrangement of the neighbouring irons with antiparallel magnetic moments. A relatively high positive correlation was obtained when arrangement of all the cations in the neighbourhood was considered. In this case, the cross-correlation coefficient is in the region

of 0.70–0.78 (variations of the cross-correlation coefficient correspond to various choices in cases of ambiguous G^{hf} values — see Table).

In contrast to the cationic environment, no positive correlation with the hyperfine field anisotropy appeared for the nearest oxygen neighbourhood. As can be seen from Table, relatively high hyperfine field anisotropy was observed in the cases of a regular oxygen polyhedron and, vice versa, quite low in the case of strongly distorted one. This finding may indicate either a minor role of the covalence contribution in the anisotropic part of the hyperfine field or its strong dependence on the arrangement of the next cationic neighbourhood of the nearest oxygen anions.

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