

Hyperfine Fields and Lattice Deformations in Ba and Sr Hexaferrites

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Hyperfine magnetic fields on ^{57}Fe nuclei in Sr and Ba hexagonal ferrites are calculated in dependence on unit cell volume and c/a ratio. By analysing the local deformations of Fe–O–Fe triads the results are explained as changes to contact hyperfine field due to Fe–O covalency effects and supertransferred hyperfine fields. Most pronounced effect is found for bipyramidal iron Fe(b) where the total contact field is reduced due to noticeable shortening of Fe(b)–O bonds.

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1. Introduction

Hyperfine interactions are highly sensitive to local crystal and magnetic structure, and therefore, significant changes of hyperfine fields are expected under lattice deformations. Current electronic structure calculations are well suited for studying how the structural changes and crystal properties are linked, and thus can serve as a tool for interpretation and better understanding of experimental results. Nuclear magnetic resonance experiments in thin films of Sr hexagonal ferrite with lattice mismatch [1] have shown that additional mechanisms other than macroscopic demagnetization field contribute to the resulting spectrum. In this work we employ density functional theory calculations to study the changes of hyperfine interactions with lattice deformations of Sr and Ba M-type hexaferrites.

The hyperfine field is the sum of fields created by interactions of the nucleus with dipolar and orbital moments of on-site electrons and by Fermi contact interaction of s electrons with the nucleus, which is usually the dominant term for iron. The s electrons of iron are polarised by the on-site unpaired $3d$ electrons, and especially $4s$ are also strongly influenced by the neighbouring oxygens and irons.

2. Method

Density functional theory calculations of Sr and Ba hexaferrites were performed using the full-potential, augmented plane waves with local orbital method as implemented in the WIEN2k code [2]. The radii of atomic spheres were chosen as 2.0 a.u. for Fe, 2.5 a.u. for Sr and Ba atoms and 1.45 a.u. for oxygens (1 a.u. \approx 0.529 Å). In the wave function expansion maximum value of L was set to $L_{\text{max}} = 10$ inside the atomic spheres, while for plane wave cut off in the interstitial space $R_{\text{MT}} \times K_{\text{max}} = 6.0$ was used. The charge density Fourier series was truncated at $G_{\text{max}} = 16\sqrt{\text{Ry}}$ and the k -point sampling of

the irreducible Brillouin zone was $7 \times 7 \times 1$. For the exchange-correlation functional we employed the GGA variant of Perdew, Burke and Ernzerhof [3], and the rotationally invariant version of the LDA+ U method of Liechtenstein et al. [4] with the GGA instead of LSDA exchange-correlation potential and with single parameter $U_{\text{eff}} = U - J = 4.5$ eV applied to iron $3d$ orbitals.

For Sr and Ba hexaferrites we calculated structures with various volumes and c/a ratios near the equilibrium values. In each structure with given volume and c/a ratio the coordinates of atomic positions were relaxed with respect to minimizing the total energy and atomic forces. Subsequently, the spin-orbit coupling was introduced with magnetization parallel to the hexagonal axis in order to calculate the orbital and dipolar contributions to the hyperfine field on irons. The contact hyperfine fields on iron nuclei were evaluated using a semi-empirical method [5] based on calculated magnetic moments of $3d$ and $4s$ electrons of the Fe atoms. In addition to hyperfine fields, the dipolar fields on iron nuclei due to dipole-dipole interaction with the off-site atomic moments were calculated by direct summation within a sphere of radius 256 a.u.

Space group of M-type hexaferrite, $\text{LFe}_{12}\text{O}_{19}$, is $P63/mmc$. Large cations (L = Ba or Sr) are in 2d sites, ferric cations occupy five different crystallographic sites: octahedral 2a, 4f₂ and 12k, tetrahedral 4f₁ and bipyramidal 2b. Oxygens occupy five non-equivalent sites 4e, 4f, 6h, 12k₁, and 12k₂. The magnetic structure is collinear ferrimagnetic with easy direction of magnetization along the hexagonal axis. The magnetic moments of Fe(f₁) and Fe(f₂) are oriented opposite to those of Fe(k), Fe(a) and Fe(b).

3. Results and discussion

The dependences of total energy on c/a ratio and on volume (Fig. 1) were studied in the range of 5% change of volume and 15% of c/a , while the symmetry of the structure was kept unchanged. The calculated equilibrium lattice parameters, i.e., parameters of structure with the minimum total energy, are displayed in Table I together with experimental values. Difference between the experimental [6, 7] and the calculated unit cell volume (4.7% for

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SrM and 6.0% for BaM) is expectable since the gradient correction acts as an isotropic negative pressure, and thus GGA overestimates the volume by several percent [8]. Very good agreement of c/a ratio was reached for SrM, while the difference is larger yet below 1% for BaM.

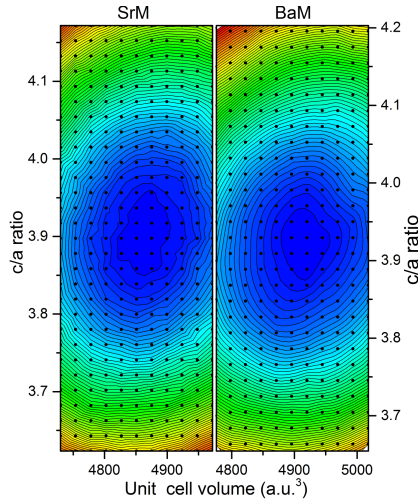


Fig. 1. Plot of total energy in dependence on unit cell volume and c/a ratio for Sr and Ba hexaferrites. Black dots represent structural parameters of the actual calculations. The step in energy, represented by lines and colour change, is 25 meV.

TABLE I

Calculated and experimental (at 4.2 K) lattice parameters, volumes and c/a ratios.

Structure	a [Å]	c [Å]	V [Å ³]	c/a
SrM (calc.)	5.9618	23.3533	718.85	3.9171
SrM (exp.) [6]	5.8758	22.958	686.43	3.9072
BaM (calc.)	5.9941	23.4315	729.09	3.9091
BaM (exp.) [7]	5.865	23.099	688.11	3.9385

Of interest are dependences of hyperfine fields on either volume or c/a ratio. Since these are not entirely independent (e.g., for high c/a deformation the most favourable volume is slightly different from the equilibrium value), we constructed the dependences as paths with minimum energy: in each point of dependence on volume we used the c/a ratio with minimum total energy and vice versa. How the hyperfine fields on iron nuclei react to changes of volume or c/a ratio is plotted in Fig. 2. The hyperfine fields on ^{57}Fe nuclei show varying dependences on c/a ratio, while the volume dependences are weak — only Fe(b) field displays mild decrease with increasing volume.

By analysing separately the dependences of individual contributions to hyperfine field on performed deformations, we found that the contribution of core $1s$, $2s$ and $3s$ electrons to contact field, orbital and dipolar terms and lattice dipolar field exhibited variations below 1%. On the other hand, the contact field due to the valence $4s$ electrons varied dramatically and was almost solely responsible for all observed changes. For explanation we analysed the impact of deformation on the local structure in more detail.

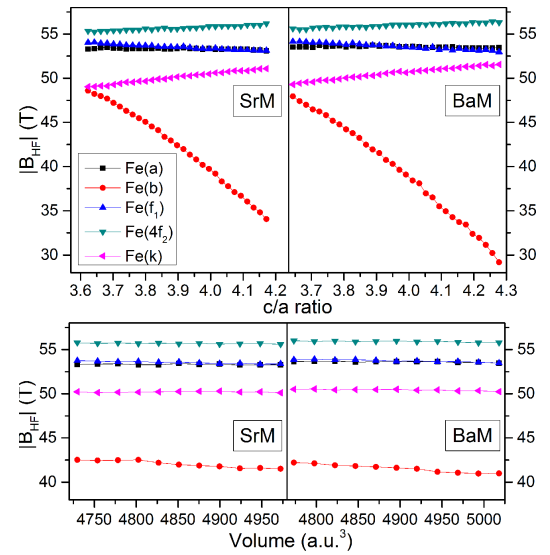


Fig. 2. Absolute values of the total hyperfine fields on iron nuclei are displayed in dependence on volume and c/a ratio of the unit cell for Ba and Sr hexaferrites.

The contribution of $4s$ electrons to the contact field arises due to supertransferred hyperfine field (STHF) and polarisation effects originating in Fe–O covalence [9, 10]. The STHF is produced by overlap of the Fe s states with oxygen orbitals (polarised by the transfer to unoccupied $3d$ states of neighbouring Fe) and by the electron transfer from $3d$ shell of the neighbouring Fe via shared oxygen ligand. Both transfers enhance the density of spins antiparallel to the $3d$ spins, and therefore, the STHF increases the total hyperfine field. The oxygen influence manifests also by two transfers: from oxygen neighbour to empty Fe $3d$ orbital and from oxygen to Fe $4s$ orbital. The first transfer must be weak in our case since the core contributions are almost intact. The latter one, however, produces strong polarisation directed opposite to the core contributions, thus effectively reducing the total hyperfine field.

In order to evaluate the impact of these contributions on hyperfine fields we have to analyse the geometry of the surroundings of the particular iron. The strong effect of Fe–O covalency on the hyperfine field is governed by the interatomic distance, while the STHF is influenced by the local geometry in a more subtle way, but in analogy with superexchange interaction. This allows us to limit our analysis to such Fe–O–Fe triads, where there is some substantial exchange interaction present. The triads in question are Fe(a)–O(k_1)–Fe(f_1), Fe(b)–O(h)–Fe(f_2), and Fe(f_2)–O(k_2)–Fe(k) where the exchange is very strong, Fe(f_1)–O(k_1)–Fe(k) and Fe(f_1)–O(f_2)–Fe(k) with intermediate strengths and perhaps also Fe(b)–O(e)–Fe(k) with rather a weak exchange interaction [11]. Table II lists how geometric properties of these triads develop throughout the full range of applied c/a deformation and in the following text we discuss how these changes affect the hyperfine fields. The analysis is done for SrM since the results for BaM are the same in essence.

TABLE II

Nearest neighbours and their numbers are displayed, together with percentage changes to bond lengths and angles in Fe–O_{NN}–Fe_{NN} triads due to 15% increase of c/a ratio of Sr hexaferrite. Triads with intermediate or weak superexchange interaction are in parenthesis. *) denotes equilibrium Fe–O distances.

Fe	# O _{NN}	Fe–O _{NN} dist. *) [Å]	Fe–O _{NN} change [%]	# Fe _{NN}	O _{NN} –Fe _{NN} change [%]	Triad angle change [%]
a	6 O(k ₁)	2.0315	+0.5	6 f ₁	-1.1	-6.9
	3 O(h)	1.8808	-3.2	6 f ₂	+1.5	-3.0
b	2 O(e)	2.2875	+14.3	(6 k)	-2.0	+6.5
	1 O(f)	1.9200	+3.1	(3 k)	-0.8	+3.4
f ₁	3 O(k ₁)	1.9264	-1.1	3 a (6 k)	+0.5 +1.2	-6.9 +3.7
	3 O(h)	2.0828	+1.5	3 b	-3.2	-3.0
f ₂	3 O(k ₂)	1.9937	-1.4	6 k	+0.3	+2.3
	1 O(e)	2.0079	-2.0	(1 b)	+14.3	+6.5
k	1 O(f)	2.1140	-0.8	(1 f ₁)	+3.1	+3.4
	2 O(k ₁)	2.1414	+1.2	(3 f ₁)	-1.1	+3.7
	2 O(k ₂)	1.9533	+0.3	2 f ₂	-1.4	+2.3

Small expansion of Fe(a) oxygen octahedron weakens slightly the covalence of the Fe–O bond and increases the total hyperfine field. This is however compensated by reducing of the STHF: lowering of the angle and increase of its bond-length asymmetry weakens the exchange polarization from neighbouring Fe(f₁). The resulting change of the contact field thus should be small, which is in agreement with constant dependence in Fig. 2.

In case of Fe(b) the three already very short Fe(b)–O(h) bonds become even shorter and more covalent, while the influence of distant O(e) can be neglected. The STHF from Fe(b)–O(h)–Fe(f₂) triad is reduced due to lower angle and increase of the asymmetry, and additionally, the weak negative effect to STHF from Fe(k) diminishes. All these effects add up and reduce strongly the total field of Fe(b).

Polyhedra of f₁ and f₂ irons deform substantially, however, the effects of Fe–O covalence quite precisely compensate. The change of the total field is thus determined by STHF, which is lowered for f₁ due to weakening of Fe(f₁)–O(k₁)–Fe(a) polarisation and raised for f₂ since the polarisation from Fe(k) is enhanced whereas the polarisation from Fe(b) is diminished only slightly.

For Fe(k) the influences of oxygen transfer again compensate and the prevailing STHF is increased due to improved interactions with f₁ and f₂ — in agreement with increase of the total hyperfine field on Fe(k) in Fig. 2.

Analogous discussion for volume deformation is more straightforward. The oxygen polyhedra are inflated and Fe–O distances increase by 1.7% on average, which decreases the covalence character of the bond and thus decreases the polarization of 4s electrons. However, this is

quite well compensated by lower STHF due to stretching of the Fe–O–Fe triads, with exception of Fe(b) where the bipyramid also elongates with increasing volume, and thus the hyperfine field slightly decreases, similarly as for c/a deformation.

Our qualitative analysis can also explain why in NMR experiment the hyperfine field of Fe(b) in BaM is by 0.9 T lower than field in SrM at 4.2 K [12]. The bipyramid in BaM is more expanded than in SrM: the key distance Fe(b)–O(h) is 1.8904 Å (1.8807 Å for SrM). In SrM structure such value would correspond to c/a ratio lower by -1.5% which would have the hyperfine field lower by about 1.4 T.

4. Conclusions

Lattice deformations of Sr and Ba hexaferrites lead to changes in valence part of the contact hyperfine field, which were explained by analysing the connection between geometry of the Fe–O–Fe triads and polarisation effects originating in Fe–O–Fe supertransfer and Fe–O covalence.

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