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Study of Y-type Hexaferrite by Means of ^{57}Fe NMR and Electronic Structure Calculations

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The electron structure and site preferences of Zn and Fe cations in Y hexaferrite system were calculated. The hyperfine magnetic fields on ^{57}Fe nuclei were determined using WIEN2k and corrections for hyperfine contact interaction. The calculated fields were compared to ^{57}Fe nuclear magnetic resonance (NMR) experiment in $Ba_2Zn_2Fe_{12}O_{22}$ single crystal with an aim of interpretation of experimental NMR spectrum.

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1. Introduction

Observation of magnetoelectric coupling in Y type hexaferrite system $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ reported by [1] rekindled interest in these hexaferrite systems. Electronic structure calculations of band gap [2] have indicated that distribution of zinc in hexaferrite structure could play an important role in emergence of magnetoelectricity. We present a study performed mainly on related Y type compound $Ba_2Zn_2Fe_{12}O_{22}$ with identical crystal structure, but without Ba-Sr disorder in large cation sublattice. Such a simplification allows us to calculate the hyperfine fields on ^{57}Fe nuclei. Comparison of calculated and measured ^{67}Zn NMR spectra was accomplished recently [3, 4].

Crystal structure of Y type hexaferrite is formed by stacking of two types of structural blocks (S and T) along hexagonal axis, one unit cell contains three formula units. Ferric ions occupy six positions, four octahedral ($3b_{VI}$ and $6c_{VI}$ in T block, $3a_{VI}$ in S block and $18h_{VI}$ shared by adjacent S and T blocks) and partially with zinc two tetrahedral ($6c_{IV}$ in S block and $6c^*_{IV}$ in T block). The Fe/Zn distribution in tetrahedral sites can be described by parameter γ: fraction γ of Zn is in S blocks, and 1-γ is in T blocks. Magnetic structure of studied Y-type hexaferrite is collinear, the moments of ferric ions in $3a_{VI}$, $18h_{VI}$ and $3b_{VI}$ sites are parallel with total magnetization (spin up), while those in $6c_{IV}$, $6c^*_{IV}$ and $6c_{VI}$ are antiparallel (spin down). Magnetocrystalline anisotropy is of easy plane type, magnetization is perpendicular to hexagonal c-axis.

2. Methods

The electronic structures of Ba and Sr hexaferrites were calculated using the augmented plane waves and local orbital method, based on the density functional theory (DFT) as implemented in the WIEN2k program [5]. For the exchange-correlation functional the generalized gradient approximation (GGA) form [6] was adopted. To improve the description of iron 3d electron correlations we used the rotationally invariant version of the LDA+U method as described by Liechtenstein et al. [7], with the GGA instead of LSDA exchange-correlation potential and with a single parameter $U_{\text{eff}} = U - J$. The radii of the atomic spheres were chosen as 2.5 a.u. for large cations (Ba, Sr), 2.0 a.u. for small cations (Fe, Zn) and 1.5 a.u. for oxygens. The number of the basis functions was 95/atom ($RK_{\max} = 6.0$), and the charge density was Fourier expanded to $G_{\max} = 16\ \sqrt{Ry}$. The number of k-points in irreducible part of Brillouine zone was 10 (20 for BaSrY case). $U_{\text{eff}} = 4.5$ eV was used for Fe and 6 eV for Zn. The atomic positions were optimized by minimizing the total energy and the atomic forces.

Single crystal sample of $Ba_2Zn_2Fe_{12}O_{22}$ was grown using Na_2O-Fe_2O_3 flux technique in Pt crucibles [8]. Frequency swept ^{57}Fe NMR spectra were recorded at 4.2 K in external magnetic fields from zero up to 1.5 T parallel with hexagonal axis of sample.

3. Results and discussion

It is well known that the DFT significantly underestimates the Fermi contact term of the hyperfine magnetic field at magnetic atoms. To correct for this error we obtained the NMR frequencies for Ba_2Y structures with $\gamma = 0$, $\gamma = 0.5$, and $\gamma = 1$ by applying procedure described in [9]. In this procedure the spin-orbit coupling was introduced which lowered the symmetry and some equivalent atoms became non-equivalent. Corrected contact field was summed with orbital and dipolar contributions to the hyperfine field and with dipolar magnetic field from the neighboring atoms (in sphere with 256 a.u. radius).

The calculated frequencies are summarized in Table I, together with frequencies for $\gamma = 0.65$ obtained from $\gamma = 0.5$ and $\gamma = 1$ by linear interpolation. One should note from Table I that the crystal sites are influenced differently by γ; the resonance frequency of $3a_{VI}$ and $3b_{VI}$ lines depends strongly on γ while e.g., $18h_{IV}$ is practically unaffected. The value $\gamma = 0.65$ is taken from our previous ^{67}Zn NMR study [4] and matches well with a value of $\gamma = 0.62$ that would yield the best agreement for our current ^{57}Fe NMR data.

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TABLE I

Calculated resonance frequencies (in MHz, gyromagnetic ratio of ^{57}Fe is 1.38 MHz·T^{-1}) for several values of γ and assigned resonance frequencies in experimental ^{57}Fe NMR spectra

Fe site	$\gamma = 0$	$\gamma = 0.5$	$\gamma = 1$	$\gamma = 0.65$	NMR
$6c_{IV}(1)$	(zinc)	70.37	72.65	71.05	69–70
$6c_{IV}(2)$	74.08	74.44	(zinc)	74.44	71–73
$6c_{VI}(1)$	74.07	74.38	71.41	73.49	71–73
$6c_{VI}(2)$		72.49		72.17	71–73
$3a_{VI}$	76.13	71.62	66.76	70.16	74.5
$18h_{VI}(1)$	68.80	67.72	68.87	68.07	69 ± 2
$18h_{VI}(2)$		68.72		68.76	
$18h_{VI}(3)$	69.72	69.46	69.62	69.51	69 ± 2
$18h_{VI}(4)$		70.87		70.49	
$18h_{VI}(5)$	68.65	69.92	68.09	69.37	69 ± 2
$18h_{VI}(6)$		69.61		69.15	
$3b_{VI}$	68.90	73.70	80.92	75.87	77.0

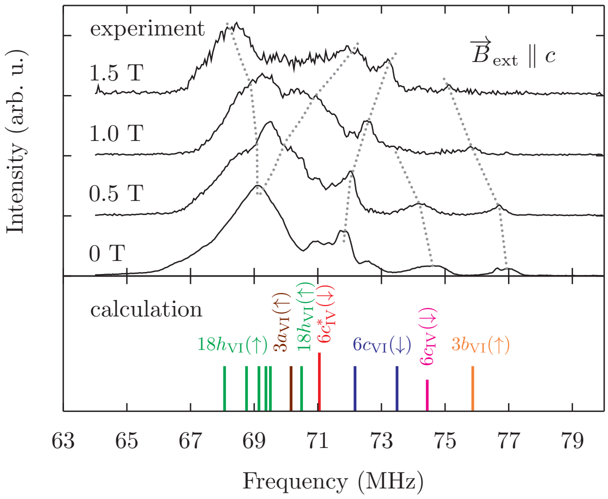

Fig. 1. Top: experimental ^{57}Fe NMR spectra of Ba_2Zn_2Y in external magnetic fields up to 1.5 T at 4.2 K, dotted gray lines indicate shifts of resonance frequencies. Bottom: calculated resonance frequencies for $\gamma = 0.65$, height of the lines is proportional to NMR intensity. (See text for details).

The calculated frequencies for $\gamma = 0.65$ are displayed in Fig. 1 together with the experimental ^{57}Fe NMR spectra. By comparison of calculated frequencies with the NMR experiment we are able to assign all spectral lines to crystallographic positions. For the assignment we also used information on the spin orientation of individual sublattices from the shifts of spectral lines in applied external magnetic field. Shift to higher frequencies with increasing field indicates spin down sublattice and vice versa. We interpret the strong and broad signal centered at 69 MHz as overlapped resonances from $18h_{VI}$, $6c_{IV}$ and $6c_{VI}$ sublattices, peak at 71.8 MHz to $6c^{*}_{IV}$ sublattice, line at 74.5 MHz to $3a_{VI}$ and the line at 77 MHz to $3b_{VI}$.

In Table II we report the calculated total energies for nine hexaferrite structures with three Ba/Sr compositions and three different values of γ. The zinc preference for $6c_{IV}$ sites is relatively independent of the large cations.

TABLE II

Calculated difference ΔE in total energy per unit cell (in eV) is displayed as a function of γ for three Ba/Sr compositions. (For a given composition, ΔE are presented relative to the value for $\gamma = 1$)

	$\gamma = 0$	$\gamma = 0.5$	$\gamma = 1$
Ba_2Y	0.40	0.17	0.00
BaSrY	0.54	0.22	0.00
Sr_2Y	0.69	0.35	0.00

4. Conclusions

We calculated the electronic structure of Ba_2Zn_2Y with various distributions of zinc between the tetrahedral sites, which allowed us to interpret the experimental ^{57}Fe NMR spectrum. The observed value of γ agreed with value obtained in previous ^{67}Zn NMR study [4].

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