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MÖSSBAUER EFFECT IN ANTIFERROMAGNETIC SUBSTANCES WITH GARNET STRUCTURES

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A number of antiferromagnetic "single lattice" garnets in which the magnetic iron ions occupy only one type of crystallographic sites – a, d, or c, are investigated. The investigations are carried out by the nuclear γ-resonance spectroscopy technique at helium and intermediate temperatures. The Néel points of the garnets and the temperature dependence of the magnetic moment of the sublattices are determined. The values of the intrasublattice exchange integrals, J_{aa}, J_{dd} and J_{cc} are estimated. Intrasublattice exchange interactions are compared for one- and two-sublattice garnets by employing various theoretical models.

INTRODUCTION

FERRITES with garnet structure constitute an extensive class of compounds having interesting magnetic properties. For example, iron garnets of rare-earth elements have three magnetic sublattices $\{R_3\}[Fe_2](Fe_3)O_{12}$ (the curly, square, and round brackets pertain respectively to the c, a, and d sublattices), and different types of intra- and interlattice exchange interactions exist in them. The strongest here is the interaction between the Fe^{3+} ions in the a and d sublattices, which determine in the main the Curie point and the temperature dependence of the magnetic moment.

It was established recently[1,2] that an important role can be played also by the intrasublattice exchange interactions (d – d and a – a). Owing to methodological difficulties, however, these interactions have been very little investigated in the garnets (see, for example,[3]).

To study the intrasublattice interactions, we can use a substitution method[4,5], in which two of the three magnetic sublattices are replaced by non-magnetic ions. The garnet becomes "single-sublattice" and its magnetic properties are determined by the exchange interaction between the magnetic ions within the sublattice. In this case the sublattice breaks up into (at least) two additional sublattices, the magnetic moments of which are antiparallel, and the garnet becomes antiferromagnetic[3].

We have investigated a large number of garnets containing magnetic iron ions in only one sublattice, d, a, or c (see the table). To investigate these compounds, we used the Mössbauer effect, the advantage of which is that it can be used to investigate the spontaneous magnetization of sublattices in antiferromagnets, and also to determine reliably the values of the Néel points. In addition, in this method the measurements are performed in a zero external magnetic field, so that no perturbations are introduced into the system by the external field.

EXPERIMENTAL PROCEDURE AND SAMPLES

The Mössbauer measurements were performed at helium and intermediate temperatures. The γ-resonance spectrometer consisted of an electrodynamic type vibrator with a feedback system, a scintillation γ-quantum detector with NaI(Tl) crystal 0.2 mm thick, and an AI-256 multichannel analyzer. The vibrator together with the γ-quantum source (Co^{57} in Cr) was placed in a cryostat and had a temperature close to that of liquid nitrogen. The investigated samples were secured on a copper plate connected by a cold finger to the helium bath, and were located in vacuum. A heating coil was wound on the same plate. Such a system made it possible to obtain any temperature in the range from 5.5 to 300°K. The temperature was stabilized during the experiment by an electronic stabilizer and maintained constant within less than 0.1°K during the experiment. The temperature was measured with a high-purity indium-wire resistance thermometer glued to the copper plate. The resistance of the indium thermometer was monitored with an R-309 potentiometer.

Polycrystalline samples of the investigated garnets (see the table) were synthesized by a ceramic technology from the corresponding oxides and carbonates. Antimony was introduced into the charge in the form of Sb_2O_3 and was oxidized by slow heating in air to the pentavalent modification.

An x-ray analysis has demonstrated the absence of extraneous phases. The parameters of the primitive cubic cell and the conditions for obtaining the samples are given in the table.

In the investigation of the Mössbauer spectra and in the paramagnetic region we have found that the Fe^{3+} ions occupy only one type of crystallographic position[8]. This confirmed experimentally the "single-sublattice nature" proposed for these garnets on the basis of crystal-chemistry considerations[5].

Above the Néel temperature, the Mössbauer spectra of all the garnets are quadrupole doublets. The quadrupole splitting parameters Δ and the values of the isomer

Certain characteristics of garnets containing magnetic iron ions in only one tetrahedral (d), octahedral [a], or dodecahedral {c} sublattice

Garnet	Synthesis temperature, °C	a_0, Å±0.003	T_N, °K	$\lvert J_{ii} \rvert$, °K	H_{eff} (0° K), kOe	Δ, mm/sec ±0.015	δ, mm/sec ±0.015
$Na_3Te_2(Fe_3)O_{12}$	775	12.524 *	67	2.88	445	0,505	0.490
$NaCa_2Sb_2(Fe_3)O_{12}$**	1230	12,600	47	2.01	447	0.810	0.475
$Ca_3SnSb(Fe_3)O_{12}$***	1350	12.634	40	1.72	475	0.955	0.480
$GdCa_2Sn_2(Fe_3)O_{12}$	1400	12,666	34.5	1.48	470	0,945	0,470
$Ca_3ZrSb(Fe_3)O_{12}$***	1400	12.669	11	0.47	450	0.985	0,490
$Ca_3[Fe_2]Si_3O_{12}$	Hydro-therm. [7]	12,070	~10	~0,217	~550	0.575	0.640
$Cd_3[Fe_2]Ge_3O_{12}$	1150	12.263	<7	<0.152	—	0.33	0,610
$Ca_3[Fe_2]Ge_3O_{12}$	1230	12,322	12,6	0.276	545	0.345	0.685
$\{Fe_3^{2+}\}Al_2Si_3O_{12}$	Natural	11.520	7,6	0,475	240	3.54	1,565

Note. a_0—unit cell parameter, T_N—Néel temperature, $\lvert J_{ii} \rvert$—exchange integral, H_{eff}—effective magnetic field at Fe^{57} nucleus, Δ—quadrupole splitting parameter, δ—isomeric chemical shift.

*A value a_0 = 12.386Å is given erroneously in [6] for the garnet $Na_3Te_2Fe_3O_{12}$.

**We also synthesized at 1300–1350°C an aluminum analog of this compound $NaCa_2Sb_2Al_3O_{12}$ (a_0 = 12.318 ± 0.004Å) (see [4]).

***The Fe^{3+} in these garnets can be replaced by Ga^{3+}. We synthesized also $Ca_3TiSbGa_3O_{12}$ (synthesis temperature 1375°C; a_0 = 12.440 ± 0.003Å), $Ca_3SnSbGa_3O_{12}$ (1300 – 1375°C; a_0 = 12.538 ± 0.003Å), $Ca_3ZrSbGa_3O_{12}$ (1375–1400°C; a_0 = 12.576 ± 0.004Å).

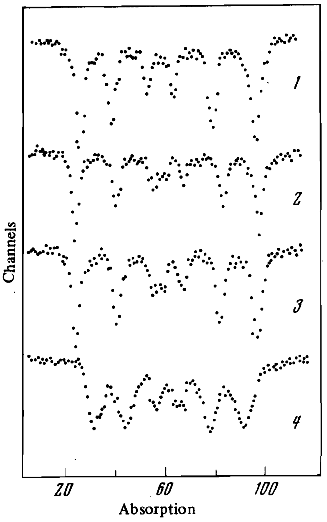

FIG. 1

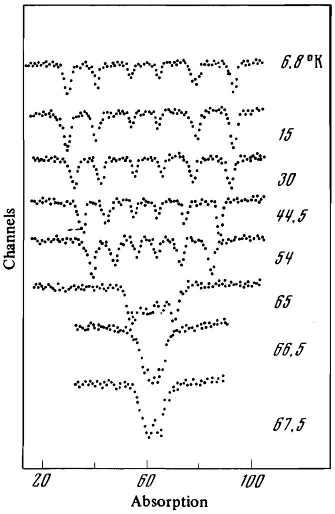

FIG. 2

FIG. 1. Mössbauer spectra of certain garnets containing magnetic Fe^{3+} ions in the d-sublattice, in the antiferromagnetic region (T = 6.8° K). 1–$GdCa_2Sn_2 \cdot (Fe_3)O_{12}$, 2–$NaCa_2Sb_2(Fe_3)O_{12}$, 3–$Ca_3SnSb(Fe_3)O_{12}$, 4–$Ca_3ZrSb(Fe_3)O_{12}$.

FIG. 2. Mössbauer spectra of the garnet $Na_3Te_2(Fe_3)O_{12}$ at temperatures near the Néel point.

shift δ at room temperature are listed in the table. The values of Δ and δ for the a-sublattice differ appreciably from the corresponding values for the d-sublattice, as is typical of the garnet structure[8].

RESULTS AND DISCUSSION

1. d-sublattice. Figure 1 shows the Mössbauer spectra of some of the investigated garnets containing Fe^{3+} ions only in the tetrahedral d-sublattice. At temperatures considerably below T_N, the spectra are split by the magnetic hyperfine interaction into six components corresponding to a single value of the field H_{eff} at the nuclei of all the Fe^{3+} d-ions. The spectral lines are somewhat broadened by the quadrupole interaction. The distances between the first and second spectral lines, on the one hand, the fifth and sixth, on the other, are not equal in most garnets. This indicates that the magnetic moments of the Fe^{3+} d-ions in the "single-sublattice" garnets do not lie in the [111] direction, unlike the yttrium iron garnet, where the direction of the easy magnetization coincides with [111].

For arbitrary orientation of the magnetic moment relative to the crystallographic axes, the Mössbauer spectrum should consist of two Zeeman sublevels that differ in the observed values of the quadrupole splitting[9]. This is probably the cause of some line broadening.

Figure 2 demonstrates the characteristic change in the Mössbauer spectra when the Néel point is approached. The spectra of certain garnets exhibit near T_N an anomaly in the form of an intense peak in the central part (see Fig. 6). Such effects can apparently be connected with singularities of the fluctuations of the magnetic moments near the phase-transition temperature, for example with the "critical superparamagnetism" phenomenon discussed by Levinson et al.[10]

Figure 3 shows the temperature dependence of the effective magnetic field H_{eff} at the C^{57} nuclei for all garnets with iron ions in the d-sublattice. This dependence was used to determine the Néel point values listed in the table. The values of T_N for different garnets with magnetic ions in the d-sublattice differ quite strongly. For example, for the garnet $Na_3[Te_2](Fe_3)O_{12}$ we have T_N = 67° K, whereas for $Ca_3[ZrSb](Fe_3)O_{12}$ the value of T_N is nearly 11° K. Note that the values of T_N correlate with the change of the lattice parameter a_0 (see the table), namely, T_N decreases with increasing a_0.

It is presently customary to assume that the effective

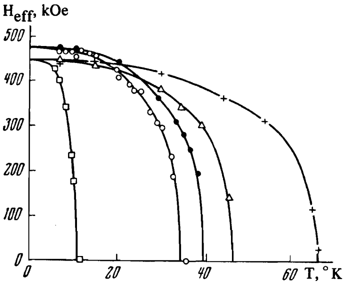

FIG. 3

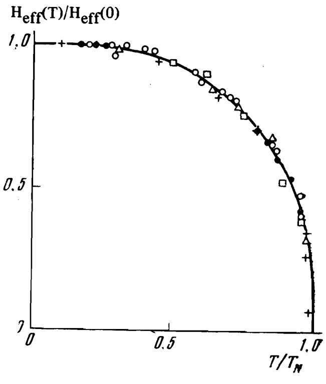

FIG. 4

FIG. 3. Temperature dependence of the effective magnetic field H_{eff} at the nuclei of the Fe^{3+} ions in the d-sublattice of garnets. +—$Na_3Te_2(Fe_3)O_{12}$, ○—$GdCa_2Sn_2(Fe_3)O_{12}$, ●—$Ca_3SnSb(Fe_3)O_{12}$, Δ—$NaCa_2Sb_2(Fe_3)O_{12}$, □—$Ca_3ZrSb(Fe_3)O_{12}$.

FIG. 4. Experimental dependence of the relative effective field $H_{eff}(T)/H_{eff}(0)$ on the relative temperature T/T_N for single-sublattice garnets with magnetic d-sublattice (the points correspond to the same garnet as in Fig. 3). The solid line shows the theoretical curve in accordance with Eq. (1).

magnetic field H_{eff} at the Fe^{3+} nuclei is proportional, as a function of the temperature, to the magnetization σ of that sublattice in which this ion is located (i.e., $H_{eff}(T)/H_{eff}(0) = \sigma(T)/\sigma(0)$). We have plotted the effective field against the temperature in the reduced coordinates $\tilde{H} = H_{eff}(T)/H_{eff}(0)$, $\tilde{T} = T/T_N$ (Fig. 4). It turned out that the $\tilde{H}(\tilde{T})$ plots for all the garnets with magnetic ions in the d-sublattice fall, with experimental accuracy, on a single curve. The solid line in Fig. 4 shows the curve obtained from the molecular-field theory in accordance with the equation (see[11])

$$\frac{\sigma}{\sigma_0} = B_S\left(\frac{3S}{S+1}\,\frac{\sigma/\sigma_0}{T/T_N}\right), \qquad (1)$$

where B_S is the Brillouin function for the spin $S = 5/2$, and there is no external field. We see that the experimental points for all the garnets fit the experimental curve well. It can apparently be assumed that the molecular-field theory describes well the temperature dependence of the magnetization of such "single-sublattice" garnets. Relation (1) provides us with a method of extrapolating the experimental $H_{eff}(T)$ plot to $T = 0°K$ and to $T = T_N$.

Knowing the experimental values of the Néel temperature T_N, we calculated the exchange integrals J_{dd} characterizing the intrasublattice exchange interaction between a pair of nearest magnetic ions. In the molecular-field theory, the exchange integral for antiferromagnets can be estimated from the relation

$$J_{ii} = \frac{3kT_N}{2z_{ii}S(S+1)}. \qquad (2)$$

Here $i \equiv d$, $z_{dd} = 4$ is the number of nearest magnetic neighbors, and k is Boltzmann's constant. The values of J_{dd} are listed in the table.

One of the garnets considered, namely $GdCa_2Sn_2(Fe_3)O_{12}$ contains, in addition to magnetic Fe^{3+} ions in the tetrahedral sublattice, also magnetic Gd^{3+} ions in the c-sublattice. Therefore, strictly speaking, it cannot be regarded as a single-sublattice garnet. However, the results of Atzmany et al.[12], who measured the c-d and c-c interactions in gadolinium iron garnets, and the fact that only one-third of the c-points is occupied by gadolinium ions (the rest of the c-points are occupied by diamagnetic ions), indicate that gadolinium should have a weak effect on the magnetic behavior of the d-sublattice.

2. a-sublattice. The garnets investigated by us, with magnetic Fe^{3+} ions in one a-sublattice, are also listed in the table. The garnet $Ca_3Fe_2Ge_3O_{12}$, prepared by a ceramic method, reveals a distinct magnetic phase transition at 12.6°K (see Figs. 5 and 6). We note that measurements of the magnetic susceptibility of this compound did not make it possible to establish uniquely the value of the Néel temperature[3]. The dependence of the effective magnetic field on the temperature is shown in Fig. 5.

Samples of the garnets $Cd_3Fe_2Ge_3O_{12}$, prepared both by a ceramic and by a hydrothermal method, remained paramagnetic down to 7°K.

The garnet $Ca_3Fe_2Si_3O_{12}$ was obtained under hydrothermal conditions[7,13]. The spectra of this garnet revealed at low temperature a magnetic hyperfine splitting that disappears at ~ 10°K. Near this temperature, the spectra have a complicated form and cannot be uniquely interpreted. This may be due to a certain deviation from the chemical composition, due to the hydrothermal preparation procedure.

From the experimental value of the Néel point, we have determined by means of formula (2) (where $z_{aa} = 8$) the values of the exchange integral J_{aa} for the garnet $Ca_3Fe_2Ge_3O_{12}$ (see the table). For the garnet $Cd_3Fe_2Ge_3O_{12}$ we present an upper estimate, and in the case of $Ca_3Fe_2Si_3O_{12}$ the value of J_{aa} can be given only with some uncertainty.

We note that in samples having Fe^{3+} ions in the a-sublattice there is no correlation between the lattice

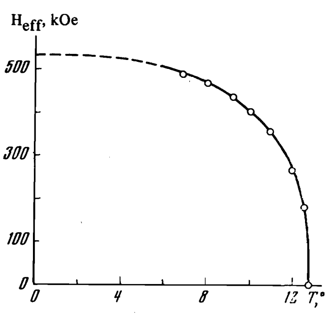

FIG. 5

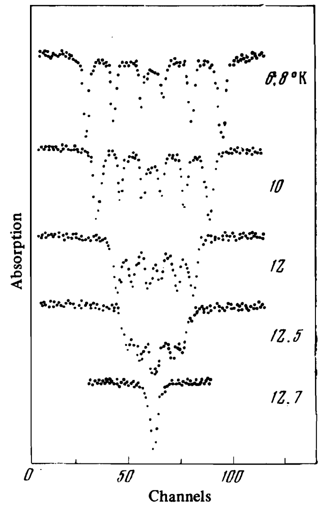

FIG. 6

FIG. 5. Temperature dependence of the effective magnetic field H_{eff} for the garnet $Ca_3[Fe_2]Ge_3O_{12}$.

FIG. 6. Mössbauer spectra of the garnet $Ca_3[Fe_2]Ge_3O_{12}$ at different temperatures.

parameter, the Mössbauer parameters Δ and δ, and the Néel temperature (see the table).

3. c-sublattice. Crystals with garnet structure usually contain ions of trivalent iron in the octa- and tetrahedral sites, and the c-sites are usually occupied by large ions of rare earths, yttrium, calcium, sodium, etc. A unique position is occupied by the natural garnet-structure mineral almandine, in which the iron is in a divalent state and occupies a dodecahedral c-sublattice. The chemical formula of almandine is $\{Fe_3^{2+}\}Al_2Si_3O_{12}$[4]. In the paramagnetic region of temperatures, the Mössbauer spectra of almandine have the form of a doublet with a very large quadrupole-splitting parameter Δ, equal to 3.82 mm/sec at 7°K. With further lowering of the temperature, a magnetic hyperfine structure appears in the spectra. We obtained 5.5 ± 0.1°K for the Néel point of this garnet.

The maximum content of Fe^{2+} ions in almandine is ~ 43 wt.% (from the FeO content). In the natural minerals, however, it is lower as a rule. In the almandine investigated by us, the FeO content was 31% (as given by chemical analysis), i.e., the magnetic c-sublattice was partially diluted by nonmagnetic ions. This dilution can apparently be interpreted as a decrease in the number of nearest magnetic neighbors by a factor ~ 31/43. The Néel temperature of the "ideal" garnet $\{Fe_3^{2+}\}Al_2Si_3O_{12}$ should then be ~ 7.7°K. This is close to the value $T_N = 7.5°K$ obtained by Prantle[14] from measurements of the magnetic susceptibility (Prantle does not give the chemical analysis of the almandine).

The value of the exchange integral J_{cc} listed in the table for the Fe^{2+} ions in the garnet c-sublattice corresponds to the "ideal" compound $\{Fe_3^{2+}\}Al_2Si_3O_{12}$.

4. Comparison of the parameters J_{ii}. It is of interest to compare the values of the intra-sublattice exchange interactions J_{aa} and J_{dd}, obtained by us for "single-sublattice" garnets, with the corresponding values for yttrium iron garnet $Y_3[Fe_2](Fe_3)O_{12}$, which has two magnetic a- and d-sublattices. The values of J_{aa} and J_{dd} for yttrium iron garnet, obtained from an analysis of the spontaneous-magnetization and paramagnetic-susceptibility curves by the molecular-field method, are $J_{aa} \approx 10°K$ and $J_{dd} \approx 16°K$[15,16]. These values are smaller by approximately one order of magnitude than the values obtained by us (see the table). Such a discrepancy in the exchange parameters is due to a shortcoming of the molecular-field theory when applied to ferrimagnets. As shown by Smit and Wijn[17], it overestimates the interactions inside the sublattices, and particularly inside the sublattice with the lower magnetization.

Information on the exchange interactions can be obtained also from the Landau-Lifshitz exchange rigidity constant D, which enters in the dispersion equation for the spin waves. For rare-earth iron garnets, the dispersion law of the acoustic branch of the spin waves can be written in the form[18,19]

$$\hbar\omega = Da^2k^2$$

(a is the lattice constant and k is the wave vector). The value of D, however, still does not give the exchange integrals, but only their linear combination. Thus, for example, for yttrium iron garnet we have[19]

$$D = {}^5/_{16}(8J_{aa} - 5J_{ad} + 3J_{dd}).$$

To find the exchange integrals it is necessary to know the relation between J_{aa}, J_{dd}, and J_{ad}.

The constant D for the yttrium iron garnet was determined experimentally by measuring the low-temperature specific heat[18] and nuclear magnetic resonance[20]. Data by different authors on the specific heat give a rather large spread in the constant D (from 24 to 41°K)[21]. The most reliable are apparently the NMR results[20], from which it follows that D is equal to 43.2°K, and the experimental data are best described by the theoretical curve at the following values of the exchange integrals:

$$J_{ad} = 32.4 \pm 1.4° K, \quad J_{dd} = 2.9 \pm 0.7° K; \quad J_{aa} = 0.7 \pm 0.7° K.$$

This value of J_{ii} agree satisfactorily with our data and apparently reflect correctly the order of magnitude of the intra-sublattice exchange interactions in iron garnets.

We note also that the values of J_{dd} and J_{aa} obtained by us are close to the estimates of Wojtowicz[22], obtained from an analysis of the magnetic susceptibility of yttrium iron garnet by the method of high-temperature expansions.

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