EXCHANGE INTERACTIONS IN COBALT GARNETS

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Magnetization curves of cobalt-containing rare-earth and yttrium garnets are measured at temperatures between 1.5 and 100°K and in fields up to 60 kOe. It is shown that the a–d exchange interaction of the Co^{2+} ions is much smaller than the a–a and c–a interaction for Co^{2+}–Co^{2+}. It is found experimentally that the R^{3+}–Co^{2+} (c–a) exchange interaction may change the nature of the magnetic ordering in cobalt garnets from that of antiferromagnetic (R–Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}) to ferromagnetic ordering (R–Er^{3+}, Yb^{3+}). An estimate of the exchange interaction parameter for Co^{2+}–Co^{2+} in the a sublattice yields a value which is greater than the exchange interaction parameter for R^{3+}–R^{3+} in the same sublattice by almost two orders of magnitude.

THE magnetic properties of rare-earth garnets containing in place of Fe^{3+} the ions Co^{2+}, Ni^{2+}, Mn^{2+} and other IIIA ions have so far been little investigated.[1] Cobalt garnets are apparently of special interest from the point of view of the theory of magnetic ordering, since the Co^{2+} ion is the only magnetic ion large quantities of which enter into any of the three magnetic sublattices of the garnet. It is at the same time possible in this case to investigate the magnetic exchange interactions of the sharply anisotropic rare-earth ions with the anisotropic Co^{2+} ion which has a nonzero orbital moment.

We present below the results of measurements of the magnetic properties of synthesized polycrystalline rare-earth and yttrium garnets containing cobalt ions in one (the a sublattice), two (the a and d sublattices), and three (a, d, and c) magnetic sublattices.

THE SAMPLE AND THE EXPERIMENTAL METHOD

The initial components for the preparation of the samples were rare-earth and yttrium oxides (with a purity no worse than 99.95%), Co_3O_4 (analytically pure), GeO_2 (spectroscopically pure), and $CaCO_3$ (All-union standard purity). The carefully ground mixtures were pressed into samples in the form of small pointers ($60 \times 3 \times 4$ mm) and were annealed in air in accordance with previously chosen temperature regimes (see the table) in the course of 9–10 hours. The phase composition of the samples was determined from x-ray patterns obtained on a URS-50IM diffractometer (cobalt radiation with an iron filter and SI-4R counter). The lattice constants (see the table) were determined from reflections in the 70–83° angular range.

Garnets of the composition $R_3 Co_{2.5} Ge_{2.5} O_{12}$ where R is a rare-earth ion are formed with the Nd–Lu row and with yttrium. The Co^{2+} ions in these garnets are both in the a and d sites, however the exact distribution of the Co^{2+} is unknown. It can only be assumed that an increase in the dimension of the R^{3+} ion "requires" larger a ions, i.e., the distribution will tend towards the form $\{R_3\}[Co_2](Co_{0.5} Ge_{2.5})O_{12}$ with R–Nd^{3+}, and Sm^{3+}. In the case of R^{3+} ions having a smaller ionic radius the fraction of Co^{2+} ions in d sites may increase

somewhat with a corresponding quantity of Ge^{4+} going over into a sites. In any event, in all these compounds no less than 20% of the Co^{2+} ions are in d sites.

The Co^{2+} ion can also occupy the c site in garnets.[2] We prepared samples containing Co^{2+} ions in all three sublattices. In the system $\{Y_{3-2x} Co_{2x}\} Co_{2.5-x} Ge_{2.5+x} O_{12}$ single-phase garnets with x = 0.1, 0.2, 0.3, and 0.4 were obtained. The garnet $\{CaY_2\}[Co_2](Ge_3)O_{12}$ in which the Co^{2+} ions are only in the a sublattice was also synthesized.[3]

We measured for all samples in the 1.5–100°K temperature range by the induction method the specific magnetization isotherms from whose initial linear section we determined the magnetic susceptibility. Temperatures above 4.2°K were obtained with the aid of a glass insert filled with heat-exchange gaseous helium (at a pressure of about 1 mm Hg) and a heater wound on the sample; an Au + Co–Cu thermocouple was used to measure the temperature. The magnetization of the samples in the entire temperature range was carried out with the aid of a superconducting solenoid which made it possible to obtain magnetic fields up to 60 kOe (at temperatures below 4.2°K the critical field of the solenoid decreased somewhat). In order to increase the accuracy with which the magnetic susceptibility was de-

Lattice constants, conditions of preparation, and the magnetic characteristics of the investigated garnets

Composition	a_0 (± 0.002 Å)	Sintering temperature °C	Θ_N ($\pm 0.1°$ K)	T = 4.2° K		T = 1.6° K	
				H_c^{**} Oe	σ_r, gauss-cm³/g	H_c Oe	σ_r, gauss-cm³/g
$Sm_3Co_{2.5}Ge_{2.5}O_{12}$	12.520	1330	8.0	--	--	--	--
$Eu_3Co_{2.5}Ge_{2.5}O_{12}$	12.485	1350	6.4	--	--	--	--
$Gd_3Co_{2.5}Ge_{2.5}O_{12}$	12.460	1370	--	--	--	--	0.7
$Tb_3Co_{2.5}Ge_{2.5}O_{12}$	12.422	1370	2.5	10	0	100	0.7
$Dy_3Co_{2.5}Ge_{2.5}O_{12}$	12.389	1370	2.0	10	0	110	1.4
$Ho_3Co_{2.5}Ge_{2.5}O_{12}$	12.359	1370	1.7	10	0.24	100	3
$Er_3Co_{2.5}Ge_{2.5}O_{12}$	12.330	1370	--	15	0.16	320	3.7
$Tu_3Co_{2.5}Ge_{2.5}O_{12}$	12.302	1370	--	10	0	10	0.2
$Yb_3Co_{2.5}Ge_{2.5}O_{12}$	12.275	1370	--	10	0.1	700	1.75
$Lu_3Co_{2.5}Ge_{2.5}O_{12}$	12.256	1350	7.5	--	--	--	--
$Y_3Co_{2.5}Ge_{2.5}O_{12}$	12.354	1335	8.1	--	--	--	--
$\{CaY_2\}[Co_2]Ge_3O_{12}$	12.350 *	1335	7.8	--	--	--	--
$\{Y_{2.8}Co_{0.2}\}Co_{2.4}Ge_{2.6}O_{12}$	12.334	1330	4.5	--	--	--	--
$\{Y_{2.4}Co_{0.6}\}Co_{2.2}Ge_{2.8}O_{12}$	12.290	1330	1.8	--	--	--	--
$\{Y_{2.2}Co_{0.8}\}Co_{2.1}Ge_{2.9}O_{12}$	12.268	1330	--	--	--	--	--

*The accuracy with which a_0 is determined amounts to ± 0.005 Å.
**H_c is the coercive force.

termined at temperatures below 4.2°K, the magnetization isotherms were also recorded in weak magnetic fields (up to 2 kOe) which were produced by a water-cooled pancake solenoid.

RESULTS AND DISCUSSION

In the $Y_3 Co_{2.5} Ge_{2.5} O_{12}$ garnet the non-magnetic Ge^{4+} ions occupy mainly d sites. This fact, as well as the fact that the magnetic moment of the Co^{2+} ion in the garnet structure (3.7 μ_B) is less than the magnetic moment of the Fe^{3+} ion (5 μ_B) leads to a decrease in the a–d interaction. Therefore in this garnet the intrasublattice interaction of the Co^{2+} ions in the a sublattice which according to [4] is of an antiferromagnetic nature becomes dominant.

In Fig. 1 we present the temperature dependences of the molar susceptibility which we obtained for yttrium–cobalt garnets. For the $\{CaY_2\}[Co_2]Ge_3 O_{12}$ sample in which the Co^{2+} ions only enter into the a sublattice one observes on the magnetic susceptibility curve $\chi_m(T)$ a maximum at 7.8°K which is due to the antiferromagnetic ordering of the Co^{2+} ions in this sublattice. The Néel point (Θ_N) for the garnet $Y_3 Co_{2.5} Ge_{2.5} O_{12}$ (curve 5) in which part of the Co^{2+} ions ($\sim 20\%$) enters into the d sublattice also occurs at about the same temperature (8.1°K). This attests to the fact that in yttrium–cobalt garnets, unlike in iron garnets, the a–d interaction is smaller than the intrasublattice a–d interaction. Indeed, the garnet $\{Y_{0.5} Ca_{2.5}\} [Fe_2] (Fe_{0.5} Si_{2.5}) O_{12}$ is according to [5] a ferromagnet with a Curie point of 86°K.

In order to determine the magnitude of the $Co^{2+}-Co^{2+}$ interaction in a sublattice of a garnet one can, as was shown in [6], make use of the Rushbrooke–Wood formula:[7]

$$\frac{k\Theta_N}{|I|} = \frac{k\Theta_c}{|I|}\left[1 + \frac{2}{3zS(S+1)}\right],$$

where Θ_N and Θ_C are the points of the antiferromagnetic and ferromagnetic transitions, I is the exchange integral, z is the number of nearest neighbors, S is the value of the spin, and k is the Boltzmann constant.

Since the determination of I is in the nature of an estimate, using the relation

$$\Theta_C = 1.1 zS^2(I/k),$$
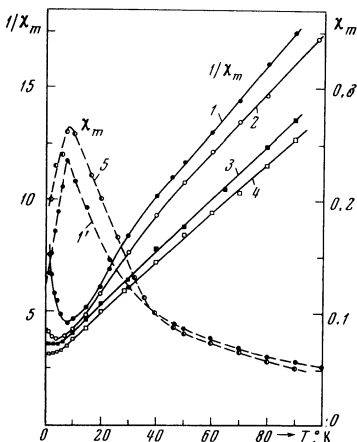
obtained for a Heisenberg ferromagnet,[8] we obtained

FIG. 1. Temperature dependence of the molar susceptibility (χ_m and $1/\chi_m$) for yttrium-cobalt garnets: 1,1'–$\{CaY_2\}$ $[Co_2](Ge_3)O_{12}$, 2–$\{Y_{2.8}Co_{0.2}\}$ $Co_{2.4}Ge_{2.6}O_{12}$, 3–$\{Y_{2.4}Co_{0.6}\}$ $Co_{2.2}Ge_{2.8}O_{12}$, 4–$\{Y_{2.2}Co_{0.8}\}$ $Co_{2.1}Ge_{2.9}O_{12}$, 5– $Y_3 Co_{2.5} Ge_{2.5} O_{12}$.
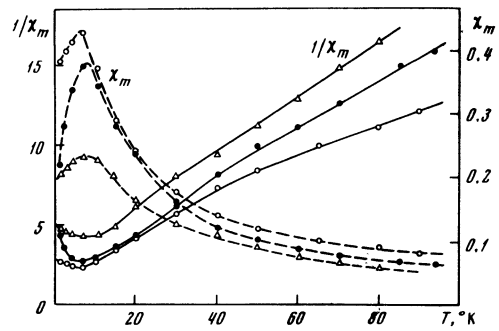

FIG. 2. Temperature dependence of χ_m and $1/\chi_m$ of Eu, Sm, and Lu cobalt garnets: O–$Eu_3 Co_{2.5} Ge_{2.5} O_{12}$, ●–$Sm_3 Co_{2.5} Ge_{2.5} O_{12}$, Δ–$Lu_3 Co_{2.5} O_{12}$.
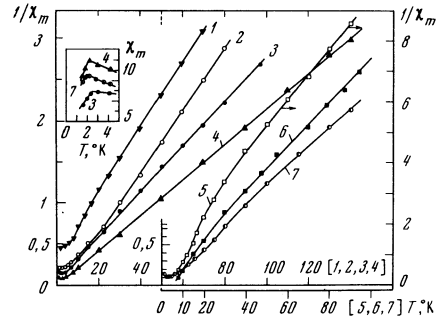

FIG. 3. Temperature dependence of $1/\chi_m$ and χ_m of rare-earth cobalt garnets $R_3 Co_{2.5} Ge_{2.5} O_{12}$: 1–R–$Tu^{3+}$, 2–R–$Gd^{3+}$, 3–R–$Tb^{3+}$, 4–R–$Dy^{3+}$, 5–R–$Yb^{3+}$ (right-hand ordinate axis), 6–R–Er^{3+}, 7–R–Ho^{3+}.

for the garnet $\{CaY_2\}[Co_2](Ge_3)O_{12}$ a value of the exchange parameter $I_{aa}/k = 3.2°K$ (z = 8 for ions in the a sublattice of garnet). We note that a calculation of the exchange parameter by the molecular field method from the $\chi_m^{-1}(T)$ curve yields for the same sample $I_{aa}/k = 3.5°K$. These values are almost by a factor of two and one-half smaller than the value of 8.3°K obtained in [9] for the $Fe^{3+}-Fe^{3+}$ interaction in the a sublattice of yttrium iron garnet.

The introduction of cobalt, even in small quantities, into the c sublattice of Y–Co garnets leads to a considerable lowering of the Néel point (curves 2 and 3, Fig. 1); for the sample $\{Y_{2.2}Co_{0.8}\} Co_{2.1}Ge_{2.9}O_{12}$ (curve 4) Θ_N lies apparently already in the region of ultralow temperatures. Such a sharp weakening of the $Co^{2+}-Co^{2+}$ interaction in the a sublattice is obviously due to the effect of the a–c interaction. The a–c interaction in cobalt garnets is considerably stronger than the a–d interaction. True, the lattice parameter of samples containing cobalt in the c sublattice is somewhat smaller than in $Y_3 Co_{2.5} Ge_{2.5} O_{12}$ (see the table) and this, as has been shown above, can lead to a decrease in the number of Co^{2+} ions in the a sublattice, and consequently to a weakening of the a–a interaction. However, our measurements have established that in the $Lu_3 Co_{2.5} Ge_{2.5} O_{12}$ sample which has the smallest lattice parameter of all the garnets studied by us the Néel point is observed at 7.5°K. Thus, in Y–Co garnets containing Co^{2+} in all three sublattices the a–c interaction between the cobalt ions is the strongest interaction.

The replacement of Y^{3+} ion in cobalt garnets by the

rare-earth ions Sm^{3+}, Eu^{3+}, and Lu^{3+} does not change the nature of the magnetic ordering at low temperatures. As is seen from Fig. 2, the $Sm_3Co_{2.5}Ge_{2.5}O_{12}$, $Eu_3Co_{2.5}Ge_{2.5}O_{12}$, and $Lu_3Co_{2.5}Ge_{2.5}O_{12}$ samples have Néel points at 8.0, 6.4, and 7.5°K respectively. Consequently, when the c sublattice of the cobalt garnets contains the nonmagnetic Y^{3+} and Lu^{3+} ions or the "weakly magnetic" Sm^{3+} and Eu^{3+} ions, then the dominating a–a interaction of the Co^{2+} ions at low temperatures leads to the antiferromagnetism of these garnets.

When Tb^{3+}, Dy^{3+}, and Ho^{3+} ions are introduced into the c sublattice the Néel point of the corresponding cobalt garnets is lowered (Fig. 3), and a residual magnetization σ_r is observed in them at 1.5°K; the latter is apparently connected with the metamagnetic state of these samples below Θ_N. Our measurements have
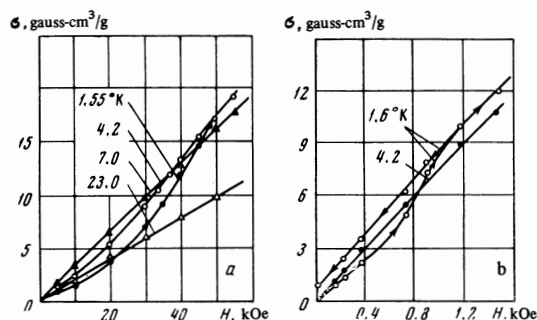

FIG. 4. Isotherms of the specific magnetization of garnets: a—for $\{CaY_2\}Co_2(Ge_3)O_{12}$, b—for $Tb_3Co_{2.5}Ge_{2.5}O_{12}$ (in weak fields).

shown that in all the investigated antiferromagnetic cobalt garnets below Θ_N one observes a metamagnetic transition when the external magnetic field reaches a certain critical H_C. The value of H_C depends on the temperature and is 40–50 kOe for a $\{CaY_2\}[Co_2]Ge_3O_{12}$ sample at T = 1.55°K (Fig. 4a). For the garnet $Tb_3Co_{2.5}Ge_{2.5}O_{12}$ ($\Theta_N = 2.5$°K) H_C does not exceed 700–800 Oe at T = 1.6°K (Fig. 4b). In the case of the garnets $Y_3Co_{2.5}Ge_{2.5}O_{12}$ and $Sm_3Co_{2.5}Ge_{2.5}O_{12}$ which have the highest Néel points (see the table) an external field of 60 kOe was obviously insufficient for reaching H_C.

It is seen from Fig. 3 (curves 5 and 6) that the temperature dependences of the reciprocal molar susceptibility for cobalt erbium and ytterbium garnets have a small concavity facing the abscissa axis. This fact, as well as the appearance of a considerable spontaneous magnetization in these garnets on cooling to helium

temperatures allows one to assume that the magnetic ordering in $Er_3Co_{2.5}Ge_{2.5}O_{12}$ and $Yb_3Co_{2.5}Ge_{2.5}O_{12}$ is of a ferrimagnetic nature.

The garnets $Gd_3Co_{2.5}Ge_{2.5}O_{12}$ and $Yu_3Co_{2.5}Ge_{2.5}O_{12}$ remain paramagnetic in the entire temperature range investigated by us (Fig. 3, curves 1 and 2). Thus, the introduction into the c sublattice of rare-earth ions from Tb^{3+} to Yb^{3+} leads to a decrease of the antiferromagnetic a–a interaction and to the appearance of a R^{3+}–Co^{2+} interaction which leads to ferrimagnetism. In the case of Er and Yb garnets this interaction becomes dominant. The R^{3+}–Co^{2+} interaction is considerably weaker than the a–c Co^{2+}–Co^{2+} interaction, since even a small addition of cobalt to the c sublattice of the garnet leads to a destruction of antiferromagnetism in the a sublattice (see the table). Such a conclusion can also be drawn with respect to the a–a interaction. As our investigations of germanium garnets containing a rare-earth ion in the a sublattice have shown,[10] the R^{3+}–R^{3+} interaction in this sublattice amounts to about 0.10°K, i.e., it is by more than an order of magnitude smaller than the Co^{2+}–Co^{2+} interaction in this sublattice. The reason for such a discrepancy lies apparently in the features of the electron structure of the Co^{2+} and R^{3+} ions which must be taken into account in estimating the intersublattice interactions in garnets.

[1] M. A. Gilleo and S. Geller, J. Phys. Chem. Solids 10, 187 (1959).

[2] S. Geller and C. E. Miller, Acta Cryst. 13, 179 (1960).

[3] D. Reinen, Z. anorg. allgem. Chem. 327, 238 (1964).

[4] S. Geller, H. J. Williams, G. P. Espinoza, and R. C. Sherwood, Phys. Rev. 136, A1650 (1964).

[5] S. Geller, J. Appl. Phys. 37, 1408 (1966).

[6] G. S. Rushbrooke and P. J. Wood, Mol. Phys. 6, 409 (1963).

[7] C. Domb and M. F. Sykes, Proc. Roy. Soc. A240, 214 (1957).

[8] D. G. Onn, H. Meyer, and J. P. Remeika, Phys. Rev. 156, 663 (1967).

[9] R. Aleonard, I. C. Barbier, and R. Pauthenet, Compt. rend. 242, 2531 (1956).

[10] K. P. Belov, B. V. Mill, V. I. Sokolov, and Than Duc Hien, Fiz. Metallov i Metallovedenie 27, 610 (1969).

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