Specific heat and magnetic properties of the antiferromagnetic garnet $NaCa_2Co_3V_3O_{12}$

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Antiferromagnetic ordering in the garnet $NaCa_2Co_2V_3O_{12}$, due to the Co^{2+}–Co^{2+} interaction in the octahedral sublattice ($T_N = 6.40$ 0.05°K) was investigated in the temperature interval 2–20°K by measuring the magnetic susceptibility and the specific heat in external magnetic fields up to 45 kOe. Estimates were obtained for the exchange-interaction integrals: $J_1/k = 02.94$°K, and $J_2/k = -1.81$°K; a splitting $\Delta_0 = 8.8$ cm^{-1} of the lower doublet of the octahedral ion Co^{2+} by the exchange field was obtained at $T = 0$°K, and the magnetic phase diagram was calculated. The experimental results obtained from measurements of the magnetic susceptibility, the magnetization, and the specific heat were found to be in good agreement within the framework of the molecular field theory with allowance for the interaction of the second neighbors for $NaCa_2Co_2V_3O_{12}$.

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1. INTRODUCTION

Belov et al.[1,2] have described the synthesis and an investigation of the magnetic susceptibility of a polycrystalline garnet, the only magnetic sublattice of which (octahedral) consists of Co^{2+} ions. It was established that antiferromagnetic order takes place in the cobalt garnet at helium temperature as a result of the Co^{2+}–Co^{2+} interaction within the sublattice. The structure of $NaCa_2Co_2V_3O_{12}$, which is made up of two ferromagnetic sublattice antiferromagnetically imbedded in each other (ordering of the first kind in accordance with Smart's classification[5]), was determined at 4.2°K from neutron diffraction data[3,4]. The $NaCa_2Co_2V_3O_{12}$ lattice parameter, according to[1], is $a_0 = 12.431$ Å. Thus, each Co^{2+} ion has eight nearest neighbors at a distance 5.383 Å, six second neighbors at 6.215 Å, and 12 third neighbors at 8.790 Å.

The mechanism of negative exchange interaction, which causes the antiferromagnetism of garnets with "one" magnetic sublattice, has hardly been investigated so far. In contrast to a two-sublattice ferrimagnet (say, $Y_3Fe_5O_{12}$), the indirect exchange interaction of the magnetic cations in the compound $NaCa_2Co_2V_3O_{12}$ is realized apparently via two O^{2-} anions. A study of the NMR with ^{51}V in the garnet $NaCa_2Co_2V_3O_{12}$ has shown that the vanadium ion does not take part in the exchange.[6]

According to the detailed investigations, by Sturge et al.[7], of the EPR of Co^{2+} in single-crystal $Y_3Ga_5O_{12}$, the octahedral ion of cobalt in the crystal field of the garnet is characterized by the split energy level scheme shown in Fig. 1. At helium temperatures, the lower

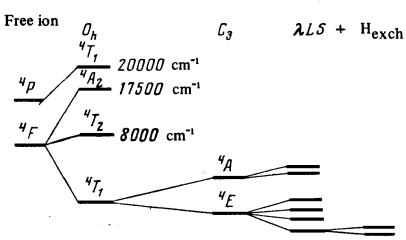

FIG. 1. Energy level schemes of the Co^{2+} ion in the octahedral sites of the garnet.

Kramers doublet is populated, so that to describe the properties of $NaCa_2Co_2V_3O_{12}$ we can use a spin Hamiltonian with effective spin 1/2:

$$\mathcal{H} = g\mu_B H_0 s + 2\sum_{i>j} s_i J_{ij} s_j + AIs, \quad (1)$$

where H_0 is the external field, g is the spectroscopic splitting factor, μ_B is the Bohr magneton, s is the effective spin, J_{ij} is the exchange integral, I is the nuclear spin (7/2), and A is the hyperfine splitting parameter ($\sim 300 \times 10^{-4}$ cm^{-1}[7]).

The main parameters characterizing the interaction of the Co^{2+} ion with the crystal field at 4.2°K are the splitting 10Dq = 8000 cm^{-1} by the cubic field, the parameter Δ_t = 650 cm^{-1} of the trigonal crystal field, and the spin-orbit splitting λ = 200 cm^{-1}. We note that investigations of the optical spectra of the $NaCa_2Co_2V_3O_{12}$ garnet yield a much larger trigonal splitting, Δ_t = 1050 cm^{-1},[8] and an inverted scheme of the splitting of the ^4T level in low-symmetry fields: the lower level is ^4A, and not ^4E as shown in Fig. 1.

To study the singularities of the antiferromagnetic transition and to obtain information on the exchange interaction, we have performed magnetic and calorimetric measurements of the polycrystallin garnet $NaCa_2Co_2V_3O_{12}$.

2. MEASUREMENT PROCEDURE

The $NaCa_2Co_2V_3O_{12}$ sample was prepared by the usual ceramic technology in the form of pressed polycrystalline pellets of density 3.6 g/cm^3, diameter $\approx$10 mm, and height h $\approx$ 3 mm. The phase composition was monitored by x-ray diffraction. There were no impurity lines on the diffraction patterns of the investigated samples.

The heat capacity was measured in the temperature interval 2–18°K with a previously described setup[9], using a vacuum calorimeter with a mechanical heat switch. The weight of the measured sample was 12.5 g. The temperature was measured with an Allen-Bradley carbon thermometer (1/8 W, $R_{300°K}$ = 50 cm) and was determined from the Clement-Quinnel formula[10]

$$1/T = A/\log R + C\log R + B. \quad (2)$$

The numerical coefficients A, B, and C were obtained from calibration of the thermometer against the vapor

pressures of liquid hydrogen and liquid helium. To measure the heat capacity in an external magnetic field, we used a superconducting solenoid, which produced magnetic fields up to 45 kOe axially homogeneous along the sample within 2%. The resultant error in the determination of the heat capacity was 1.5% at 4°K and did not exceed 3% at T = 18°K.

The magnetic susceptibility in the interval 2–70°K was determined from the magnetization isotherms, which were measured by an induction method[2] in fields up to 20 kOe on cylindrical samples from the same batch as used for the heat capacity. At 4.2°K the dependence of the magnetic moment on the external field was measured in pulsed magnetic fields up to 250 kOe by Yu. F. Popov in the Magnetism Problems Laboratory of the Moscow State University.

3. EXPERIMENTAL RESULTS

Figure 2a shows the experimental temperature dependence of the heat capacity of cobalt garnet in the interval 2–18°K in the absence of a magnetic field. The observed λ anomaly of the heat capacity corresponds to antiferromagnetic ordering of the Co^{2+} in an octahedral sublattice. The Néel temperature of the garnet $NaCa_2Co_2V_3O_{12}$ is $T_N = 6.40 \pm 0.05$°K.

At low temperatures, the investigated garnet is a magnetic insulator and its heat capacity should be defined as

$$C = C_{lat} + C_{mag} + C_{nuc}. \quad (3)$$

According to our estimate, the contribution of the nuclear heat capacity at T = 2°K is 3% of the total heat capacity of the garnet, so that the contribution of C_{nuc} can be neglected in the investigated interval 2–18°K. The dependence of $CT^2/2R$ on T^5. Shown in Fig. 3, indicates that the relation

$$C/2R = a/T^2 + bT^3 \quad (4)$$

is well satisfied in the interval 11–18°K (R is the universal gas constant), with coefficients

$$a = 27.0 \pm 0.3 \text{ deg}^2, \quad b = (31.1 \pm 0.5) \cdot 10^{-6} \text{ deg}^{-3}. \quad (5)$$

The second term in (4) determines the lattice heat capacity; the obtained value of the coefficient b yields for the Debye temperature of $NaCa_2Co_2V_3O_{12}$ the value $\Theta_D = 433 \pm 25$°K. The obtained Debye temperature agrees well with the value of Θ_D determined by us from measurements of the diamagnetic garnet $NaCa_2Zn_2V_3O_{12}$. The lattice heat capacity is shown in Fig. 2a by a dashed line. As to the first term of (4) (which we shall denote by C_1), it usually determines the magnetic contribution to the heat capacity at $T \gg T_N$. Since an estimate of the dipole interactions in garnets[11] shows that $C_{dip}T^2/R$ does not exceed 0.1 $(°K)^2$, it might be assumed that C_1 is governed only by dipole interactions. However, as seen from Fig. 2b, the entropy reaches a value corresponding to the theoretical R ln(2s + 1) for s = 1/2 already at 16°K. This obviously indicates that at 16°K the lower Kramers doublet is fully populated and that the higher-lying doublet becomes populated with increasing temperature. Therefore the heat capacity of C_1 below T_N will contain, besides the contribution from exchange interactions, also a contribution connected with transitions to lower levels.

This is evidenced by the values of the internal energy and entropy listed in the table. It is seen that whereas below T_N the values of $(S_N - S_0)/2R$ and $(E_0 - E_N)/2RT_N$ agree well with the theory, the experimentally obtained $(S_\infty - S_N)/2R$ and $(E_N - E_\infty)/2RT_N$ greatly exceed the theoretical values for the Heisenberg model of an antiferromagnet.

The internal energy and entropy were calculated with the aid of the usual relations

$$\frac{E}{2R} = \int_0^T \frac{C_1}{2R} dT, \quad \frac{S}{2R} = \int_0^T \frac{1}{2R} \frac{C_1}{T} dT. \quad (6)$$

The scale is chosen here in such a way that S/2R = 0 at T = 0 and E/2R = 0 at T = ∞. Extrapolation to the temperature region 0–2°K was carired out under the assumption that the law $C_{mag} \propto T^3$, obtained from spin-wave theory for the heat capacity of antiferromagnets at $T \ll T_N$, is valid here. The variation of the heat capacity at T > 18°K was calculated in accord with the T^{-2} law.

Figure 3a shows the temperature dependence of the reciprocal molar susceptibility of the garnet $CaCa_2Co_2V_3O_{12}$. We see that starting with 26°K a change takes place in the slope of $\chi_m^{-1}(T)$, and this obviously corresponds to population of the higher-lying levels of the Co^{2+} ion in the crystal field.

Assuming that in the interval 8–26°K the temperature dependence of the susceptibility obeys the Curie-Weiss law $\chi = C/(T - \Theta)$, we obtained $\Theta = -17.5 \pm 2$°K and C = 4.76 $cm^3 deg\text{-}mole^{-1}$. The obtained value of C yields for the effective magnetic moment of Co^{2+} a value $\mu_{eff} = 4.36\ \mu_B$, which corresponds to a g-factor (for s = 1/2)

$$g = \mu_{eff}/\sqrt{s(s+1)} = 5.0. \quad (7)$$

The obtained value of the g-factor is in good agreement with the data of[7], where they obtained for the octahedral Co^{2+} ion in YGaG the values $g_{\parallel} = 7.027$ and $g_{\perp} = 2.665$, so that for the polycrystal $g = (g_{\parallel}^2/3 + 2g_{\perp}^2/3)^{1/2} = 4.6$. The paramagnetic Curie temperature and T_N are close to the values obtained from measurements of the magnetic susceptibility of single-crystal $NaCa_2Co_2V_3O_{12}$ in the interval 2–30°K.[14] However, the magnitude and behavior of the susceptibility (Fig. 4b) below the Néel point differ somewhat from the data obtained earlier.[1,14]

Figure 5 shows the measured heat capacity of $NaCa_2Co_2V_3O_{12}$ in the absence of a magnetic field and in fields H = 20, 30, 40, and 45 kOe. (In order not to clutter up the figure, only a part of the experimental points used to plot $C_H(T)$ is shown.) It was established that the

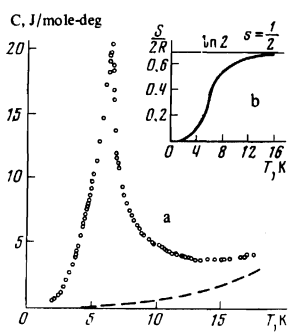

FIG. 2

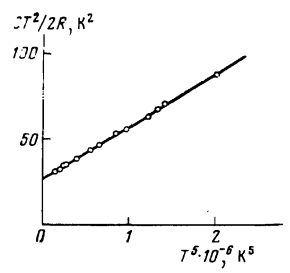

FIG. 3

FIG. 2. a) Temperature dependence of the heat capacity of the garnet $NaCa_2Co_2V_3O_{12}$ (points) and the lattice contribution (dashed line); b) temperature dependence of the entropy.

FIG. 3. Dependence of $CT^2/2R$ on T^5 for the garnet $NaCa_2Co_2V_3O_{12}$.

	Experiment	Theory, s = 1/2		
		Heisenberg model [12,13]		Ising model [13]
		bcc	hcc	bcc
$(S_\infty - S_N)/2R$	0.34	0.235	0.265	0.107
$(S_N - S_0)/2R$	0.4	–	0.428	0.5
$(E_N - E_\infty)/2RT_N$	0.68	0.46	0.439	0.169
$(E_0 - E_N)/2RT_N$	0.3	–	0.297	0.460

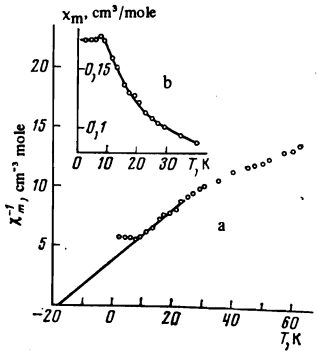

FIG. 4. Temperature dependences of χ_m^{-1} (a) and of the magnetic susceptibility (b) of the garnet $NaCa_2Co_2V_3O_{12}$.

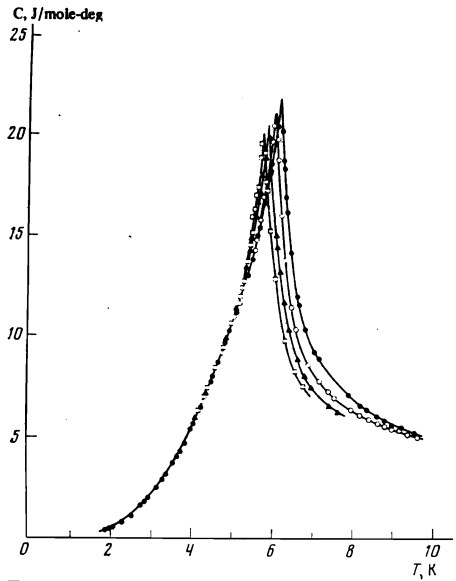

FIG. 5. Temperature dependence of the heat capacity of the garnet $NaCa_2Co_2V_3O_{12}$ in an external magnetic field: ●) H = 0, 5, 10, 20 kOe, ○) H = 30 kOe, ▲) H = 40 kOe, □) H = 45 kOe.

temperature dependences of the heat capacity, obtained in fields 5, 10, and 20 kOe coincide fully with $C_{H=0}(T)$. Starting with H = 30 kOe, the maximum of the heat capacity decreases in magnitude and shifts towards lower temperatures. It follows from our data that the destruction of the antiferromagnetic order takes place in a field H = 30 kOe at $T_N = 6.3 \pm 0.05°K$. At $H_{cr} = 40$ and 45 kOe we have $T_N = 6.1 \pm 0.05°K$ and $6.0 \pm 0.05°K$, respectively. Below ~5.2°K the temperature dependences of the heat capacity in different fields do not differ from one another.

4. DISCUSSION OF RESULTS

According to Smart[5], the body centered cubic lattice of the garnet, in the sites of which are located the magnetic Co^{2+} ions, can be broken up into four sublattices such that the ions within each sublattice do not interact (Fig. 6). Then the equations for the effective exchange fields of the sublattices take the form

$$H_1=H_0+2\gamma_1M_2+4\gamma_2M_3+2\gamma_1M_3, \quad H_2=H_0+2\gamma_1M_1+2\gamma_1M_4+4\gamma_2M_3$$
$$H_3=H_0+2\gamma_1M_1+4\gamma_2M_2+2\gamma_1M_4, \quad H_4=H_0+4\gamma_2M_1+2\gamma_1M_2+2\gamma_1M_3. \quad (8)$$

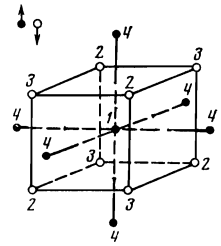

FIG. 6. Magnetic structure of $NaCa_2Co_3V_3O_{12}$.

Here $H_{i=1,2,3,4}$ is the effective field produced at the i-th sublattice by the atoms in the other sublattices; H_0 is the external field; $M_{i=1,2,3,4}$ is the magnetization of the i-th sublattice; γ_1 and γ_2 are the coefficients of the molecular field from the first and second nearest neighbors, determined for the entire sublattice. In our case,

$$|M_1|=-|M_2|=-|M_3|=|M_4|, \quad (9)$$

therefore T_N and Θ are connected with the coefficients of the molecular field in the following manner:

$$\Theta=C(\gamma_1+\gamma_2), \quad T_N=-C(\gamma_1-\gamma_2). \quad (10)$$

Using the values of Θ, C, and T_N obtained by us, we get

$$\gamma_1=-2.51 \text{ cm}^{-3}\cdot\text{mole}, \quad \gamma_2=-1.16 \text{ cm}^{-3}\cdot\text{mole}. \quad (11)$$

The relation

$$\gamma_{ij}=2zJ_i/2Ng^2\mu_B^2, \quad (12)$$

where z is the number of neighbors and N is Avogadro's number, makes it possible to determine the exchange-interaction integrals J_1 and J_2 for the first and second neighbors. For g = 5 we obtain

$$J_1/k=-2.94 \text{ K}, \quad J_2/k=-1.81 \text{ K}. \quad (13)$$

It should be noted that the obtained values of the exchange integrals are much larger than for the corresponding $Fe^{3+}-Fe^{3+}$ interaction[15] and $Ni^{2+}-Ni^{2+}$ interaction[16] in the octahedral sites of the garnet.

The contribution of the exchange interactions to the heat capacity can be estimated by using the high-temperature expansion method. At $T \gg T_N$, according to Abragam and Bleaney[17]

$$C_{exch}=\frac{R}{T^2}\frac{1}{2}\left\{\frac{s(s+1)}{3k}\right\}^2\sum_{i>j}(J_{xx}^2+J_{yy}^2+J_{zz}^2). \quad (14)$$

Allowance for only the isotropic part of the exchange with the first and second nearest neighbors yields

$$\frac{C_{exch}T^2}{R}=\frac{1}{2}\frac{2s^2(s+1)^2}{3}\left[z_1\left(\frac{J_1}{k}\right)^2+z_2\left(\frac{J_2}{k}\right)^2\right]. \quad (15)$$

Substituting in (15) the values of J_1/k and J_2/k obtained above, we get for the cobalt garnet

$$C_{exch}T^2/2R=17 \text{ K}^2, \quad (16)$$

which is much less than the experimental value (5) $CT^2/2R = 27°K^2$. It is obvious that one of the causes of the increased high-temperature "tail" of the cobalt garnet heat capacity are transitions to the lower levels. In addition, anisotropic exchange can make an additional contribution to the heat capacity.

The experimental results obtained from the shift of T_N in external magnetic fields (Fig. 5) can be compared with the theoretical phase diagram of $NaCa_2Co_2V_3O_{12}$ calculated by the molecular-field method. To this end, we multiply each of the equations in (8) by the magnetization of the corresponding sublattice and then sum (with a factor 1/2, which takes into account the paired character

of the interaction). The expression obtained in this manner for the total magnetic energy of the sample in a magnetic field takes the form

$$E=-H_0M\cos\theta-{}^1/_2\gamma_1M^2\cos 2\theta-{}^1/_2\gamma_2M^2, \quad (17)$$

where M is the saturation magnetization of the sample and θ is the angle between the magnetic moment and the field. Minimizing Eq. (17) with respect to θ, we obtain for the critical fields that destroy the antiferromagnetism

$$H_{cr}(T)=-2\gamma_1M(T). \quad (18)$$

The temperature dependence of the saturation magnetization is determined by the usual formula

$$M(T)=M(0)B\left[\frac{g\mu_B s}{kT}H_{\text{eff}}\right]. \quad (19)$$

Here B(x) is the Brillouin function, and H_{eff} takes according to (8) and (9) the form

$$H_{\text{eff}}=M(-\gamma_1+\gamma_2). \quad (20)$$

The values of the critical fields calculated in this manner as functions of the temperature are shown by the continuous line in Fig. 7. For all pairs of values of H and T under the curve, the substance in the antiferromagnetic state, and in the paramagnetic state above the curve. The same figure shows the experimental points obtained from measurements of the heat capacity in a magnetic field, and the values of the antiferromagnet collapse field, which amounts to H_{cr} = 120 kOe for $NaCa_2Co_2V_3O_{12}$ at T = 4.2°K. The latter was determined from the break on the M(H) plot obtained in pulsed magnetic fields up to 250 kOe. The good agreement between the calculated $H_{cr}(T)$ and experiment is evidence that below T_N the magnetic properties of the garnet $NaCa_2Co_2V_3O_{12}$ are described sufficiently accurately by the molecular field theory.

We note that at H = 0 and T = 0 it follows from (17) that

$$E_0={}^1/_2M_0^2(\gamma_1-\gamma_2). \quad (21)$$

Substituting here γ_1 and γ_2 from (11) and M = $2NG\mu_B s$ = 28×10^3 cgs emu/mole, we obtain for the total internal energy connected with the exchange interaction the value E_0 = −53 J/mole at T = 0.

This quantity enables us to estimate the splitting Δ_0 of the Kramers doublet by the exchange field at T = 0°K, which is connected with E_0 by the relation

$$-E_0=N\Delta_0/2.$$

The factor 1/2 takes into account here the reversal of the spin direction as the electron goes to the excited level. We thus obtain Δ_0 = 8.8 cm^{-1}.

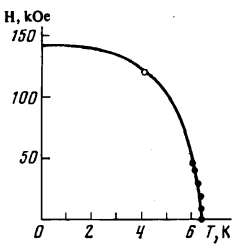

FIG. 7. Phase diagram of $NaCa_2Co_2V_3O_{12}$ sample: ●—calorimetric data, ○—from measurements of the magnetic moment in pulsed magnetic fields.

5. CONCLUSION

An investigation of the antiferromagnetic phase transition in the cubic garnet $NaCa_2Co_2V_3O_{12}$ has shown that its magnetic properties are well described with the aid of an effective spin s = 1/2 and g = 5. It was found that at T = 0°K the splitting of the doublet in the exchange field amounts to Δ_0 = 8.8 cm^{-1}. Assuming a Heisenberg exchange interaction, estimates are obtained for the integrals of the Co^{2+}—Co^{2+} exchange interaction, namely J_1/k = −2.94°K and J_2/k = −1.81°K; these turned out to be appreciably larger than the corresponding Fe^{3+}—Fe^{3+} and Ni^{2+}—Ni^{2+} interactions in the octahedral garnet lattice. The phase diagram of the antiferromagnetic $NaCa_2Co_2V_3O_{12}$, calculated by the molecular field method, agrees with experiment and yields an exchange field H_{exch} = 145 kOe at 0°K.

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