# Magnetic Properties of Aerugite $Co_{10}Ge_3O_{16}$

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**Abstract**—This paper reports on the first study of the temperature and field dependences of the magnetization, heat capacity, and electrical properties of synthesized polycrystalline samples of aerugite $Co_{10}Ge_3O_{16}$, as well as on x-ray diffraction analysis of this compound. It is shown that the cobalt ions in this compound occupy three nonequivalent positions. The results of the experimental and theoretical studies suggest that aerugite is a ferrimagnet with two uncompensated magnetic moments of the cobalt atom per formula unit.

## 1. INTRODUCTION

Recently, there has been heightened interest in compounds containing cobalt oxides. This is explained by the fact that cobalt compounds are promising materials for the development of very efficient devices, such as solid-state fuel cells, membranes for oxygen separation, and storage devices. These applications are associated with the high ionic and electronic conductivity and electrocatalytic properties of cobalt oxide compounds. In research, cobaltites can serve as model materials to gain a deeper understanding of the competing processes occurring in strongly correlated subsystems. These compounds undergo magnetic/structural/charge ordering (see, for example, [1–3]). The search for new cobalt-containing materials and investigation of their physical properties are problems of considerable importance.

In this work, the heat capacity and magnetic properties of the polycrystalline aerugite $Co_{10}Ge_3O_{16}$ were investigated for the first time.

## 2. SAMPLE PREPARATION, EXPERIMENTAL TECHNIQUES, AND CRYSTAL STRUCTURE

The initial compounds used in the synthesis were cobalt oxide $Co_3O_4$ and germanium oxide $GeO_2$ (reagent grade). The $Co_3O_4$ and $GeO_2$ oxides taken in the stoichiometric ratio were mixed, ground in an agate mortar, and pressed into pellets at a pressure of 5250 kg/cm². The polycrystals were synthesized in two

stages. The pellets were held at a temperature of 1060°C for 48 h with one intermediate grinding and pressing. As a result of these procedures, a brown-colored $Co_{10}Ge_3O_{16}$ compound was obtained.

The x-ray diffraction analysis performed on a DRON-2 setup ($CuK_\alpha$ radiation) showed that the $Co_{10}Ge_3O_{16}$ samples thus synthesized have a single-phase composition and rhombohedral symmetry $R–3m$ with the lattice parameters $a = b = 5.951$ Å, $c = 28.875$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. Aerugite has a layered structure (Fig. 1). Along the $c$ axis, this structure consists of alternating blocks of spinel and halite. The spinel block is composed of three cation layers arranged perpendicular to the $\langle 111 \rangle$ direction in the spinel. All tetrahedral sites of the spinel are occupied by $Ge^{4+}$ cations. The halite block has one cation layer perpendicular to the $\langle 111 \rangle$ direction in the halite. One-fourth of the cations in this layer are germanium cations located in octahedra.

All cobalt cations are in the divalent state and occupy octahedral positions both in the spinel and in the halite. There are three nonequivalent positions for cobalt. Let these positions be denoted as Co1, Co2, and Co3. The Co1 position is in the central layer of the spinel block and has an ideal oxygen coordination octahedron. The Co2 positions lie in the block with the halite structure and are surrounded by a slightly compressed, nearly regular oxygen octahedron. The Co3 positions are located at the boundary of the block with the spinel structure. The oxygen octahedra around these

positions are extended and have low-symmetry distortions.

The unit cell of aerugite contains 3 Co1 cations, 9 Co2 cations, and 18 Co3 cations. Thus, the formula of aerugite can be represented as $(Co1)_1(Co2)_3(Co3)_6Ge_3O_{16}$.

## 3. EXPERIMENTAL RESULTS

The electrical resistivity was measured in a zero magnetic field in the temperature range 70–300 K. The electrical resistivities at 77 and 300 K are equal to $4.32 \times 10^{10}$ and $2.56 \times 10^6$ $\Omega$ cm, respectively.

At the first stage, preliminary calorimetric measurements were performed in the temperature range 105–300 K on a DSM-2M differential scanning microcalorimeter.

The measurements performed upon both heating and cooling revealed a reproducible heat capacity anomaly at approximately 200 K. In order to determine the energy characteristics of the phase transition, an adiabatic calorimetric investigation was carried out over a wide temperature range, 60–260 K. A sample consisting of particles 0.05–0.20 g in weight was placed in a copper container and then in an indium capsule, which was evacuated and filled with helium as a heat exchange gas. The total weight of the sample was 1.92 g. The heat capacity measurements were performed upon stepwise ($\Delta T = 1.0$–2.5 K) and continuous ($dT/dt = 0.16$–0.40 K min$^{-1}$) heating.

Figure 2 plots the temperature dependence of the heat capacity of the sample + fixture system. An anomaly accompanying the phase transition is observed at $T_0 = 200.7 \pm 0.1$ K. No dependence of the position of the heat capacity maximum on the magnitude of the calorimetric step $\Delta T$ was found in the experiment. This provides a convincing argument for the absence of latent heat. Therefore, we can make the inference that the phase transition is a second-order transformation.

Now, our interest is only in the data on the anomalous heat capacity, which allows us to determine integral thermodynamic functions. The regular component in the graph depicted in Fig. 2 was determined by fitting a combined Debye–Einstein heat capacity function to the experimental data in the temperature ranges that lie above and below $T_0$ far from the transition point. The inset to Fig. 2 shows the temperature dependence of the excess heat capacity associated with the phase transition. The excess heat capacity was determined as the difference between the total (solid line) and regular (dashed line) heat capacities. Integration of the corresponding functions yielded the enthalpy $\Delta H = \int \Delta C_p dT = 2300 \pm 200$ J/mol and the entropy $\Delta S = \int (\Delta C_p/T) dT = 11.2 \pm 1.0$ J/mol K for the phase transformation. The large value of the change in the entropy $\Delta S \approx 1.4R = R\ln 4$ clearly indicates that the phase transition is accompanied by ordering.
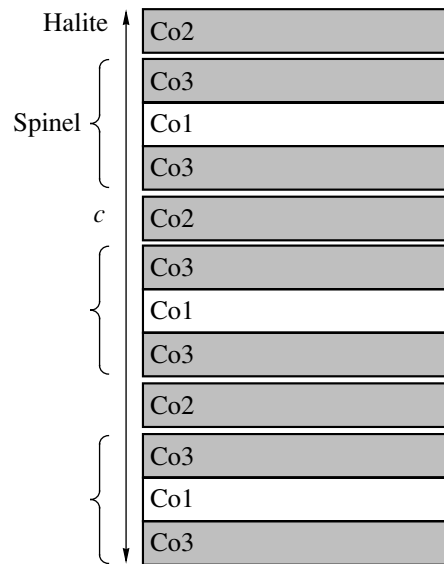


**Fig. 1.** Schematic drawing of the crystal structure of aerugite $Co_{10}Ge_3O_{16}$. Designations: Co1, Co2, and Co3 are three nonequivalent cobalt positions in the unit cell.
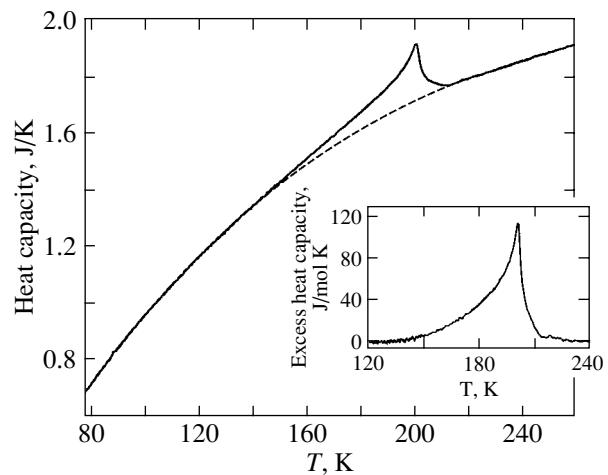


**Fig. 2.** Temperature dependence of the heat capacity of the sample + fixture system. The dashed line indicates the regular component of the heat capacity. The inset shows the temperature dependence of the excess heat capacity of the $Co_{10}Ge_3O_{16}$ compound.

A characteristic feature of the graph is a wide range of anomalous heat capacity below $T_0$. This suggests a substantial temperature dependence of the transition parameter.

The temperature and magnetic field dependences of the magnetization of polycrystalline samples were studied on a SQUID magnetometer in the temperature range 4.2–300.0 K and in fields of up to 50 kOe under
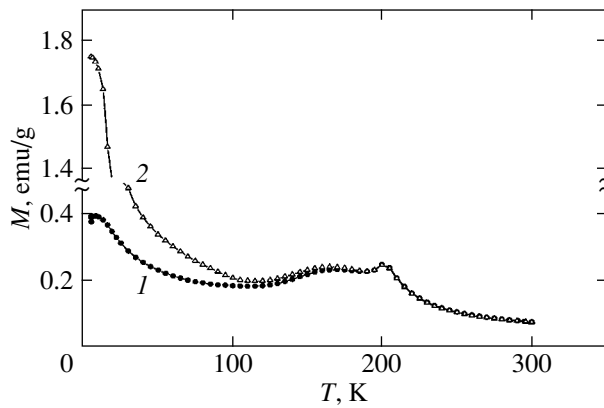
**Fig. 3.** Temperature dependences of the magnetization of the $Co_{10}Ge_3O_{16}$ samples cooled in (*1*) a zero magnetic field and (*2*) a field of 10 kOe.



**Fig. 4.** Magnetic field dependences of the magnetization of polycrystalline $Co_{10}Ge_3O_{16}$ at different temperatures.

different cooling conditions. Figure 3 displays the temperature dependences of the magnetization measured under different cooling conditions.

At $T_0 = 200$ K, there is an anomaly substantiating the existence of a magnetic phase transition. Moreover, the magnetization of a field-cooled sample (Fig. 3, curve *2*) increases drastically at temperatures below 20 K.

The field dependences of the magnetization at different temperatures are depicted in Fig. 4. Interestingly, already at temperatures below 25 K, the hysteresis loops acquire a constricted shape and the magnetizations measured at these temperatures in weak fields are considerably lower than those observed in weak fields below 20 K.

It should be noted that the field at which the hysteresis disappears increases with increasing temperature (Fig. 4).

## 4. DISCUSSION

The temperature dependences of the heat capacity and magnetic susceptibility suggest persuasively the existence of a magnetic phase transition below 200 K. The existence of a hysteresis loop allows us to conclude that a spontaneous magnetic moment appears at temperatures below 200 K. The experimental value of the spontaneous magnetic moment $M = 29.5$ emu/g at $T = 5$ K corresponds to two ferromagnetically ordered magnetic moments of $Co^{2+}$ ions. This suggests that the ferrimagnetic ordering most likely occurs in $Co_{10}Ge_3O_{16}$ at liquid-helium temperatures. In this case, six ferromagnetically coupled magnetic moments of the $Co^{2+}$ ions in a unit cell are antiferromagnetically ordered with respect to the other four ions.

In order to determine the type of the magnetic structure, we used the simple indirect coupling model developed by Anderson and Eremin [4, 5]. In this model, the
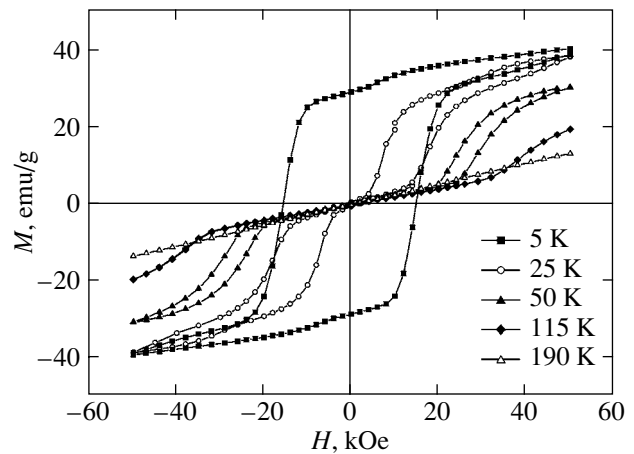
interaction of a pair of cations is represented by a sum of interactions of individual outer-electron orbitals. The orbital exchange integrals $I$ are expressed through three parameters, namely, the parameter of ligand–cation electron transfer $b$ (or $c$) along the σ (or π) bond (usually $c \approx b/2$), the ligand–cation electron excitation energy $U$, and the intra-atomic exchange integral $J^{in}$. The corresponding expressions can be written as $I = -2b^2U$ for singly occupied orbitals of adjacent cations ($\uparrow - \downarrow$), $I = +b^2J^{in}$ for empty and singly occupied orbitals ($0 - \uparrow$) and for singly and doubly occupied orbitals ($\uparrow - \uparrow\downarrow$), and $I = 0$ for empty and doubly occupied orbitals ($0 - 0$ and $\uparrow\downarrow - \uparrow\downarrow$).

We restrict ourselves to consideration of only interactions with the nearest neighbors. The electron transfer and excitation parameters for interionic distances of ~2 Å are known for the $Co^{2+}$ cation in the spinel structure [6]: $b \approx 0.026$, $c \approx 0.01$, $U = 5.6$ eV, and $J^{in} \approx 2.5$ eV.

In this case, the magnetic structure of aerugite is described by the following cation–cation exchange interaction integrals (the subscripts correspond to the numbers of the interacting sublattices in accordance with the notation of Fig. 1, the superscripts refer to the exchange coupling angle, $z$ is the number of nearest neighbors in the sublattice, and the figures in braces are the estimated values of the exchange integrals):

$$J_{11} = J_{12} = 0;$$

$$J_{13}^{90} = -2c[32bU - (8b + 3c)J^{in}]/81,$$

$$z_{13} = 6, \quad z_{31} = 1 \quad \{-11.6\ K\};$$

$$J_{22}^{90} = -4c[(8b + c)U - 2(4b + c)J^{in}]/81,$$

$$z_{22} = 4 \quad \{-3.7\ K\};$$

$$J_{23}^{90} = -c[2(8b + 3c)U - (40b + 9c)J^{in}]/81,$$

Intersublattice interactions $J_{ij}$ (in K)

| Sublattice no. | $1\downarrow$ | $2\downarrow$ | $3\uparrow$ |
|:---:|:---:|:---:|:---:|
| $1\downarrow$ | 0 | 0 | −69.6 |
| $2\downarrow$ | 0 | −14.9 | −103.4 |
| $3\uparrow$ | −11.6 | −57.7 | +12 |

$$z_{23}^{90} = 4, \quad z_{32}^{90} = 2 \quad \{-0.2 \text{ K}\};$$

$$J_{23}^{180x} = -[2(16b^2 + 3c)U - 9c^2 J^{\text{in}}]/81,$$

$$z_{23}^{180x} = 4, \quad z_{32}^{180x} = 2 \quad \{-17.5 \text{ K}\};$$

$$J_{23}^{180z} = -2[16b^2 U - 3c^2 J^{\text{in}}]/81,$$

$$z_{23}^{180z} = 2, \quad z_{32}^{180z} = -1 \quad \{-17.1 \text{ K}\};$$

$$J_{33}^{90} = -2c(3cU - 8bJ^{\text{in}})/27, \quad z_{33}^{90} = 4 \quad \{+3 \text{ K}\}.$$

These integrals allow one to determine the intersublattice interactions $J_{ij}$ (see table).

The mutual orientation of the sublattice magnetic moments due to this set of interactions is specified in the table by arrows adjoining the sublattice numbers. It thus follows that aerugite is a ferrimagnet with two uncompensated magnetic moments of the cobalt atom per formula unit and a Curie temperature $T_C = 196$ K. The interaction $J_{22}$ is frustrated.
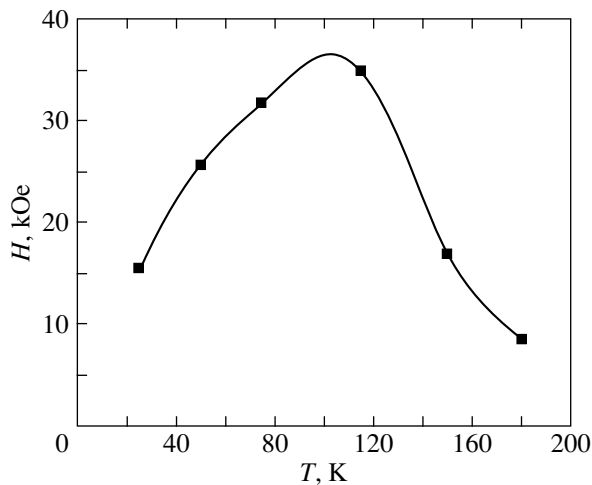


**Fig. 5.** Temperature dependence of the magnetic field corresponding to the appearance of the hysteresis loop for the $Co_{10}Ge_3O_{16}$ compound.

In our opinion, the above reasoning is valid at least for temperatures $T < 20$ K. As can be seen from the curves in Fig. 4, the hysteresis loops at higher temperatures become constricted, thus implying that, in weak magnetic fields, the spontaneous magnetic moment is zero. Note that the field at which the hysteresis loop appears depends in a nontrivial manner on the temperature (Fig. 5).

Such constricted hysteresis loops are characteristic of cobalt compounds exhibiting the so-called perminvar effect [7, 8]. The origin of the effect lies in the presence of an induced, exchange, or uniaxial magnetic anisotropy that stabilizes the direction of magnetization at all points of the crystal (both in domains and in the domain walls). If the magnetization directions in the domains and the domain walls are highly stabilized, the domain walls reside in deep potential energy wells and remain in them as the field increases to fairly high strengths. Only when the field reaches a critical value $H_c$, the domain walls become unpinned and can be displaced. A cyclic variation in the field results in the formation of a constricted or double hysteresis loop. The exchange anisotropy can also appear in ferrimagnets with a structure in which it is possible to separate two sublattices that weakly interact with the other sublattices and can be considered an antiferromagnetic subsystem. In this case, the existence of two magnetic phases is not required and one can assume that the magnetic vectors of the ferrimagnetic and antiferromagnetic subsystems are continuously distributed in space. In our case, such an antiferromagnetic subsystem can be represented by the Co1 subsystem, because its exchange with the Co2 and Co3 subsystems is weakest. Thus, if our assumption is correct, aerugite is in single-domain and multidomain ferrimagnetic states in the regions above and below the curve in Fig. 5, respectively. The magnetization peak at $T_0$ (Fig. 3) typical of the Hopkinson effect can serve as an indirect argument for the substantial contribution made by magnetic anisotropy to the magnetic properties of the $Co_{10}Ge_3O_{16}$ system.

We believe that our experimental data require additional investigation in order to verify the assumptions introduced. For this purpose, we intend to carry out elastic neutron scattering studies.

### 5. CONCLUSIONS

Thus, the heat capacity and magnetic properties of $Co_{10}Ge_3O_{16}$ polycrystals were studied for the first time. It was established that this compound undergoes a second-order magnetic phase transition at $T = 200$ K. The intersublattice and intrasublattice exchange integrals were evaluated. It was shown that the $Co_{10}Ge_3O_{16}$ aerugite is a ferrimagnet with two uncompensated magnetic moments of the cobalt atom per formula unit. The assumption was put forward that the magnetic anisot-

ropy substantially affects the magnetic properties of this compound.

## REFERENCES

1. M. Baran, V. I. Gatalskaya, R. Szymczak, S. V. Shiryaev, S. N. Barilo, K. Piotrowski, G. L. Bychkov, and H. Szymczak, J. Phys.: Condens. Matter **15**, 8853 (2003).

2. M. Baran, S. N. Barilo, G. L. Bychkov, V. I. Gatalskaya, R. Szymczak, and S. V. Shiryaev, Acta Phys. Pol., A **105**, 209 (2004).

3. D. V. Sheptyakov, A. Podlesnyak, S. N. Barilo, S. V. Shiryaev, G. L. Bychkov, D. D. Khalyavin, D. Yu. Chernyshov, and N. I. Leonuk, Paul Sherrer Inst. Sci. Rep. (Villigen, Switzerland) **3**, 64 (2001).

4. P. W. Anderson, Phys. Rev. **115**, 2 (1959).

5. M. V. Eremin, Fiz. Tverd. Tela (Leningrad) **24** (2), 423 (1982) [Sov. Phys. Solid State **24** (2), 239 (1982)].

6. O. A. Bayukov and A. F. Savitskiĭ, Fiz. Tverd. Tela (St. Petersburg) **36** (7), 1923 (1994) [Phys. Solid State **36** (7), 1049 (1994)].

7. R. Bozorth, *Ferromagnetism* (Van Nostrand, New York, 1951; Inostrannaya Literatura, Moscow, 1956).

8. S. V. Vonsovskii, Magnetism (Nauka, Moscow, 1971; Wiley, New York, 1974).

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