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MAGNETISM AND FERROELECTRICITY

Low-Temperature Magnetic Behavior of the Rare-Earth Cobaltites $GdCoO_3$ and $SmCoO_3$

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Abstract—The temperature and magnetic field dependences of the static magnetization of the polycrystalline rare-earth cobaltites $GdCoO_3$ and $SmCoO_3$ have been measured. It is shown that, below room temperature, the magnetization of both compounds derives primarily from the rare-earth ion paramagnetism. The $GdCoO_3$ and $SmCoO_3$ compounds have been found to differ substantially in magnetic behavior, which can be traced to differences in their electronic shell structures. The magnetic behavior of $GdCoO_3$ is close to that of an array of free Gd^{3+} ions, whereas in $SmCoO_3$ the deviation from the free-ion properties is very large because of the Sm^{3+} ground state being crystal-field split. Van Vleck magnetic susceptibility measurements of $SmCoO_3$ suggest that the splitting is ~10 K.

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1. INTRODUCTION

Cobaltites of rare-earth elements with the chemical formula $Ln\mathrm{CoO}_3$, where *Ln* stands for lanthanum or a lanthanide (Y, Sm, Gd, Ho, etc.), are perovskite-like crystals which have been attracting interest for a long time as materials exhibiting a variety of remarkable, largely unique properties. Among these properties are the fairly large magnetoresistance [1], anomalies in magnetic susceptibility [2, 3], thermopower [4–6], thermal lattice expansion [7], and metal–insulator transitions [8–10]. The unwaning interest in cobalt oxides stems also from their emerging applications as materials for solid-state fuel cells [11], heterogeneous catalysts, oxygen membranes, and gas sensors [12]. The fairly high thermopower generated by the cobaltites of rare-earth metals gives grounds to consider them as a viable alternative to traditional semiconducting thermoelectric materials [13].

Despite the over half-a-century long history of investigation of cobalt oxide compounds, the nature and the degree of stability of both the ground state and the higher-lying levels of Co^{3+} ions still remain a subject of intense debate [14–16]. The key issue for the rare-earth cobaltites is the so-called problem of the high-, low-, and medium spin states. A specific feature of these oxides is that the electronic states of Co^{3+} corresponding to different values of the spin S are very nearly degenerate, so that they can be coupled only by temperature or pressure. Incidentally, the question of what spin state would be realized in a particular case has still not received a clear-cut answer, neither from the theoretical nor from the experimental side.

The $LaCoO_3$ compound is at present the best studied representative of the rare-earth cobaltite family. Experimental data on other members of the $Ln\mathrm{CoO}_3$ series are still fairly scarce, particularly in the low-temperature domain. At the same time, these compounds appear quite frequently to be more efficient and promising for future applications, which justifies the study of their properties as well. We are reporting here an experimental study and a comparison of the low-temperature magnetic properties of two cobalt oxide compounds, $GdCoO_3$ and $SmCoO_3$. Despite a similarity in composition, the magnetic behavior of these two materials has revealed noticeable differences attributable to differences in the electronic shell structure of the Gd^{3+} and Sm^{3+} ions.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Our polycrystalline samples were prepared by the sol-gel method [9], by which stoichiometric amounts of nitrates of cobalt and gadolinium or samarium are dissolved in deionized water, with subsequent drying at 90°C for 6 h. The powder samples thus obtained are annealed at 300°C in air, pelletized and annealed once more. The pelletized $GdCoO_3$ and $SmCoO_3$ samples were rectangular parallelepipeds measuring $4 \times 2 \times 1$ mm.

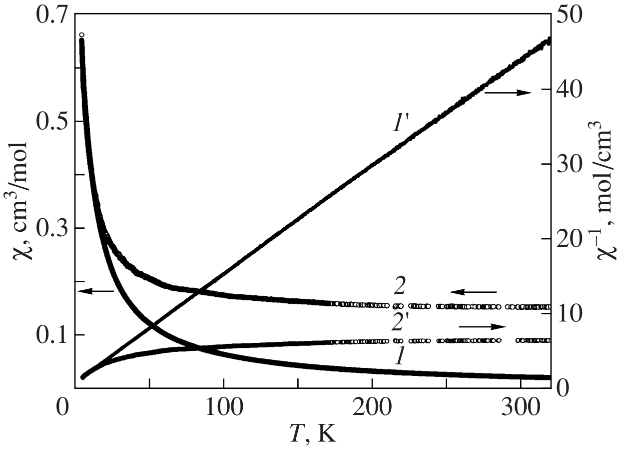

Fig. 1. Temperature dependences of the magnetic susceptibility and the inverse magnetic susceptibility for (*1*, *1*') $GdCoO_3$ and (*2*, *2*') $SmCoO_3$ in the magnetic field H = 1 kOe. The susceptibilities for $SmCoO_3$ are scaled up by a factor of 100.

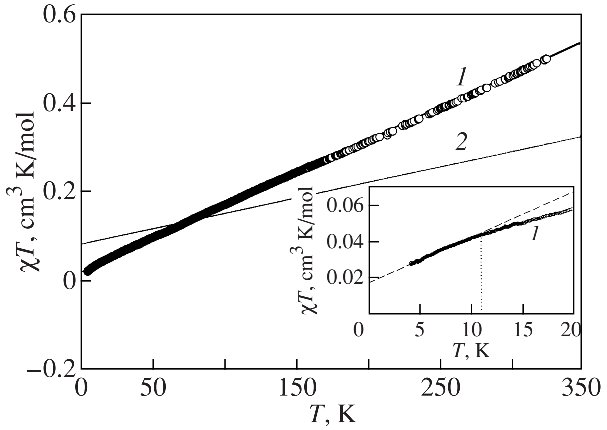

Fig. 2. Temperature dependence of the product of the magnetic susceptibility by the temperature for $SmCoO_3$ measured in the magnetic field H = 1 kOe: (*1*) experiment and (*2*) calculation for a free Sm^{3+} ion. The inset shows the low-temperature part of the graph.

We measured temperature dependences of electrical resistivity at temperatures from 80 to 400 K and of the static magnetization in the range 4.2–300.0 K, as well as magnetic-field dependences of the magnetization at different temperatures and magnetic fields of up to 70 kOe.

3. EXPERIMENTAL RESULTS

X-ray diffraction data show the structure of the samples under study to be distorted perovskite-like with P_{bnm} space group [17], which is typical of $LnCoO_3$ compounds. The lattice parameters conform to literature data [18]. The room-temperature electrical conductivity of the samples is fairly low, about 10^{-5} Ω m for $GdCoO_3$ and 10^{-6} Ω m for $SmCoO_3$. The conductivity is observed to continue to decrease with further decrease in the temperature, so that at low temperatures both compositions can be classed among insulators.

Figure 1 plots the temperature dependences of the static magnetic susceptibility χ and the inverse magnetic susceptibility χ^{-1} for $GdCoO_3$ and $SmCoO_3$ measured in a magnetic field $H = 1$ kOe. While the susceptibility of both compounds grows monotonically with decreasing temperature, one observes here three significant differences. First, the susceptibility of $SmCoO_3$ is lower in absolute value by two orders of magnitude than that of $GdCoO_3$. Second, the susceptibility of $GdCoO_3$ tends to zero with increasing temperature, and that of $SmCoO_3$, to a constant value $\chi_0 = 1.54 \times 10^{-3}$ cm³/mol. Finally, the temperature dependence of the inverse magnetic susceptibility can be fitted well by a straight line, which suggests that the Curie–Weiss law

$$\chi = C/(T + \Theta) \qquad (1)$$

holds here. This makes possible determination of the asymptotic Curie temperature $\Theta \approx -6$ K. The constant $C = \mu_{\mathrm{eff}}^2 N_A/3k = 6.81$ cm³ K/mol yields for the effective magnetic moment per formula unit $\mu_{\mathrm{eff}} \approx 7.38\mu_B$, μ_B is the Bohr magneton, N_A is the Avogadro number, and k is the Boltzmann constant. At the same time, the temperature dependence of the inverse magnetic susceptibility of $SmCoO_3$ is substantially nonlinear; hence, the Curie–Weiss law fails here.

Because the temperature dependence of the susceptibility of $SmCoO_3$ in Fig. 1 looks as a superposition of two contributions, an inversely proportional to temperature and a temperature-independent one, it appears reasonable to consider the temperature dependence of the product of the susceptibility by temperature, which in this case should be linear. This product is displayed in Fig. 2, whence it is seen that the product χT does indeed behave over a wide temperature range as a linear function of temperature. This means that the magnetic susceptibility of $SmCoO_3$ can be presented as a sum of two contributions, one of them obeying the Curie law and another, temperature-independent, χ_0

$$\chi = C/T + \chi_0. \qquad (2)$$

Approximation of experimental data with a linear relation yields $C = 2.76 \times 10^{-2}$ cm³ K/mol and $\chi_0 = 1.46 \times 10^{-3}$ cm³/mol.

The inset to Fig. 2, which shows the lowest-temperature part of the χT graph, suggests that the straight line with the above parameters has a break near T = 10–11 K and is continued by another section, also close to a linear graph. This low-temperature part of the straight line has a still steeper slope (dashed line in Fig. 2),

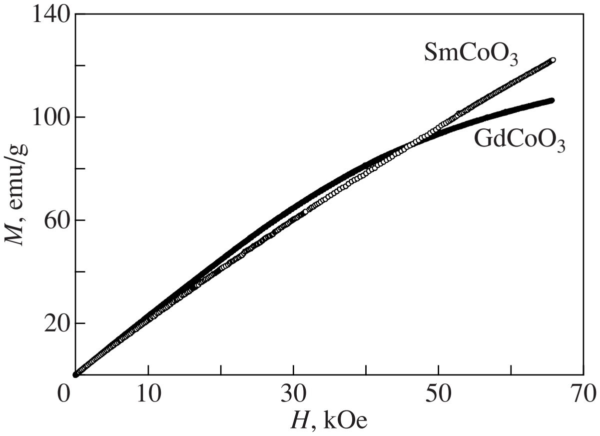

Fig. 3. Magnetization curves obtained for GdCoO$_3$ and SmCoO$_3$ at $T = 4.2$ K. The magnetizations for SmCoO$_3$ are scaled up by a factor of 100.

yielding $C = 1.68 \times 10^{-2}$ cm^3 K/mol and $\chi_0 = 2.53 \times 10^{-3}$ cm^3/mol for $T < 10$ K.

Field dependences of magnetization for both samples are linear in the weak field domain at all temperatures, a feature characteristic of paramagnets. In strong fields, however, the magnetization curves of the compositions under study behave differently. At $T = 4.2$ K and the maximum field of 70 kOe reachable in our experiment, the magnetization curve $M(H)$ of GdCoO$_3$ suggests a trend to saturation not observed in SmCoO$_3$ (Fig. 3).

4. DISCUSSION OF THE RESULTS

A question invariably arising in discussion of the properties of compounds containing magnetic ions of two kinds is the extent to which the magnetism of a particular ion accounts for the experimentally observed properties. In our case, however, experiments on structural changes [19], magnetization, and neutron spectroscopy [20, 21] seem to suggest that below room temperature Co^{3+} ions in LnCoO$_3$ compounds with Ln other than La reside typically in the low-spin nonmagnetic state. Our data on static magnetization also indicate that below room temperature Co^{3+} ions in GdCoO$_3$ and SmCoO$_3$ are in a fixed low-spin state. Thus, it is the rare-earth ions that are primarily responsible for the magnetism of GdCoO$_3$ and SmCoO$_3$ below room temperature. The above remains valid for stoichiometric compounds as well. In the case of oxygen deficiency characteristic of rare-earth cobaltites, cobalt ions induced by stoichiometry defects and residing in different valence states should certainly contribute to magnetization. Besides, even for ions in a nonmagnetic ground state the magnetic susceptibility can be not zero at all because of the presence of the van Vleck polarization component, a point to be discussed below.

The properties exhibited by magnetic ions depend predominantly on their environment, i.e., on the strength and symmetry of the crystal field. The influence of crystal field on susceptibility is most clearly pronounced in magnets in which the exchange interaction of the rare-earth ions is small as compared to the crystal field. It is to such compounds that the LnCoO$_3$ rare-earth cobaltites belong. In these compounds, the crystal-field splitting is, in order of magnitude, 10^2 cm^{-1}, which is considerably in excess of the exchange, dipole and other interactions. Gd^{3+} is in this sense an exclusion to the rule, because its ground state is the S state ($4f^7$, $^8S_{7/2}$, $L = 0$, $S = 7/2$), which is crystal field split only in higher orders of perturbation theory. Therefore, it can be expected that the Gd^{3+} ions in GdCoO$_3$ should be close in magnetic properties to an ensemble of free ions. This is what is largely observed in actual fact. Experiment reveals conventional orientational paramagnetism. We recall immediately, however, the negative value of $\Theta = -6$ K, and the noticeably smaller effective magnetic moment, $\mu_{\rm eff} = 7.38\mu_{\rm B}$, as compared to $7.94\mu_{\rm B}$ for the free ion, a feature suggesting the presence of weak antiferromagnetic interaction [17]. A similar behavior of magnetic systems with Gd^{3+} ions is characteristic also of Gd$_2$O$_3$-based oxide glasses [22–25]. For rare-earth cobaltites, small negative paramagnetic Curie temperatures were observed in La$_{1-x}$Eu$_x$CoO$_3$ compounds [26]. This experimental observation was assigned [26] to oxygen nonstoichiometry characteristic of these compounds.

The lower magnetic moment of the Gd^{3+} ion as compared to its theoretical value can also result from the crystal-field splitting of its ground state, the $^8S_{7/2}$ octet. If the ground state of ions with the half-filled 4f shell were a pure $^8S_{7/2}$, only Zeeman interaction would be nonzero. However, even in a free atom or ion, intermediate coupling plays a certain role and admixes higher lying levels to the ground state which becomes [27]

$$(1-\alpha^2)^{1/2} \times {}^8S_{7/2} + \alpha \times {}^6P_{7/2}\ldots, \tag{3}$$

where α is the admixture parameter. The ligand field splits this state, but neither the theoretical nor the experimental value of this splitting for Gd^{3+} exceeds 1 K [28].

As for the free Sm^{3+} ion, its electronic configuration id 4f^5, and its ground state is the $^6H_{5/2}$ multiplet ($L = 5$, $S = 5/2$). A characteristic feature of this ions lies in its first excited state $^6H_{7/2}$ being relatively close to the ground state. The difference between the energies of these states for a free ion is about 1000 cm^{-1}. Admixture of the excited-state wave functions to the ground state gives rise to formation of paramagnetism of a new kind, namely, polarizational van Vleck paramagnetism, which is most clearly pronounced in the Sm^{3+} and Eu^{3+} ions.

The magnetic susceptibility χ of van Vleck paramagnets can be presented as a sum of three terms

$$\chi = \chi_c + \chi_p + \chi_d, \qquad (4)$$

where χ_c is the susceptibility originating from conventional orientational paramagnetism of ground-state ions, χ_p is the polarizational van Vleck susceptibility, and χ_d is a component describing the diamagnetic contribution of electronic shells. The diamagnetic components being, as a rule, small, we shall assume it in what follows to be negligible.

The expression for molar van Vleck susceptibility can be written as [29]

$$\chi_p = 2N_\mathrm{A}\sum_{n'=1}\frac{|\langle n|\hat{M}_z|n'\rangle|^2}{\Delta'_n}, \quad \Delta'_n = E_{n'} - E_n. \qquad (5)$$

Here, N_A is the Avogadro number, M_z is the z component of the magnetic moment, and E_n and $E_{n'}$ are the ground and excited state energies. The field is assumed to be aligned with the z axis. The contribution of each term in sum (5) is the larger the smaller the energy difference $E_{n'} - E_n$. If the higher-lying levels are not thermally excited, χ_p is temperature independent.

For the Gd^{3+} ion, the energy difference between the ground, ${}^8S_{7/2}$, and the first excited, ${}^6P_{7/2}$, states is about 30000 cm^{-1}; therefore, the polarizational susceptibility is negligible, and what one observes is only the Curie–Weiss orientational contribution (Fig. 1). In Sm^{3+} ions, both susceptibility components are comparable in magnitude. The magnetic susceptibility of free Sm^{3+} ions calculated from the expression [29]

$$\chi(\mathrm{Sm}^{3+}) = \frac{\sum\limits_{J=|L-S|}^{L+S}\{[N_\mathrm{A}g_J^2\mu_\mathrm{B}^2 J(J+1)/3kT] + \chi_{p,J}\}(2J+1)\exp\left(-\frac{\Delta}{kT}\right)}{\sum\limits_J (2J+1)\exp\left(-\frac{\Delta}{kT}\right)} \qquad (6)$$

is displayed in Fig. 2 as a χT vs. T plot (curve *2*). Only two states were taken into account, the ground state with $J = 5/2$ and $g_{5/2} = 2/7 = 0.2857$, and the first excited state with $J = 7/2$ and $g_{7/2} = 0.8254$. Here, Δ was assumed to be 1100 cm^{-1} [30]. We readily see that below room temperature the graph obtained is practically linear; hence, thermal population of the ${}^6H_{7/2}$ state and the exponential terms in Eq. (6) can be neglected, and use in susceptibility calculations the simple expression (2), in which the first term accounts for the orientational, and the second, for polarizational susceptibility. For the free Sm^{3+} ion, $C = 0.0886$ cm^3 K/mol, which corresponds to an effective ion magnetic moment $\mu_\mathrm{eff} = 0.84\mu_\mathrm{B}$, and the polarizational van Vleck susceptibility at low temperatures is 6.76×10^{-4} cm^3/mol.

We thus see a pronounced quantitative difference in both orientational and polarizational susceptibility components between free Sm^{3+} ions, on the one hand, and SmCoO_3, on the other. First, the value of constant C yields an effective magnetic moment $\mu_\mathrm{eff} = 0.47\mu_B$ for the Sm^{3+} ions in SmCoO_3 at temperatures above 20 K, and only $0.37\mu_B$ below 10 K, which is substantially lower than the theoretical value of $0.84\mu_B$ for the free Sm^{3+} ion. Second, the high-temperature, temperature-independent component of susceptibility χ_p for SmCoO_3 is about twice that for the free ion, 1.46×10^{-3} against 0.676×10^{-3} cm^3/mol. At low temperatures, $T <$ 10 K, this susceptibility component reaches a still larger value, 2.53×10^{-3} cm^3/mol. Thus, the orientational contribution to the susceptibility for Sm^{3+} ions in SmCoO_3 turns out to be smaller, and the polarizational one, larger than in the case of the free ion.

Although Co^{3+} ions are in nonmagnetic state and, thus, do not contribute to orientational susceptibility, the polarizational component of their susceptibility can be not zero at all. If the ground state of the ion is nonmagnetic, and the first excited state has a magnetic moment, as is the case with the octahedrally coordinated Co^{3+}, the van Vleck susceptibility component can be calculated from the relation [26]

$$\chi(\mathrm{Co}^{3+}) = \frac{N_\mathrm{A}g^2\mu_\mathrm{B}^2}{3kT}\,\frac{\nu S(S+1)(2S+1)\exp\left(-\frac{\Delta}{kT}\right)}{1+\nu(2S+1)\exp\left(-\frac{\Delta}{kT}\right)}, \qquad (7)$$

where ν is the orbital degeneracy of the excited state. There is a problem here in that the order in which the excited states in LnCoO_3 compounds are arranged and, hence, the quantities Δ and ν, are not known precisely. Estimates made [26] from magnetic susceptibility data yielded for LaCoO_3 $\chi(\mathrm{Co}^{3+}) = 1.64 \times 10^{-4}$ cm^3/mol, and for $\mathrm{La}_{1-x}\mathrm{Eu}_x\mathrm{CoO}_3$, still smaller values. The van Vleck susceptibility of Co^{3+} in the low-spin state can be evaluated also from the isotropic component of the Knight shift ${}^{59}K_\mathrm{iso}$, which is 2.11% for SmCoO_3 [20]. One obtains from here $\chi_p(\mathrm{Co}^{3+}) \approx (4.3\text{–}4.6) \times 10^{-5}$ cm^3/mol. The corresponding correction is seen to be small, and by inserting it, we arrive for the van Vleck susceptibility of Sm^{3+} ions in SmCoO_3 at $(1.4 \pm 0.1) \times 10^{-3}$ cm^3/mol in the temperature range $20 < T < 320$ K, and at $(2.5 \pm 0.1) \times 10^{-3}$ cm^3/mol for $4.2 < T < 10.0$ K, which is again substantially larger than the free-ion value.

The reason for these differences lies in the crystal-field splitting of the Sm^{3+} ground state. In perovskite crystals, such as the orthoferrites, orthochromites, and cobaltites, the rare-earth ion resides in a low-symmetry ligand environment of symmetry C_s (distorted cuboctahedron), The field of this symmetry splits the ground state multiplet of the Sm^{3+} ion into three Kramers doublets. As shown in [31], this splitting, first, reduces the magnetic moment of the atom because of the crystal field acting on the orbital component. This feature is usually treated as "freezing" of the orbital moment, which occurs in our case too. Second, the crystal field effect can become manifest in a strong anisotropy of the g factor, saturation magnetization, and crystal susceptibility. In polycrystalline samples we deal with averaged quantities, and the magnetic susceptibility can be calculated as

$$\langle\chi\rangle = (\chi_{\parallel} + 2\chi_{\perp})/3, \tag{8}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are susceptibility components in directions parallel and perpendicular to the z axis, respectively. In the limiting case of $\chi_{\perp} = 0$, $\langle\chi\rangle = \chi_{\parallel}/3$, and the observed values of the susceptibility will be found considerably lower than those for the free ion. The anisotropy can also be a factor preventing magnetization in $SmCoO_3$ from reaching saturation.

As shown in [27, 30, 32], splitting of the Sm^{3+} ground state multiplet in fields of different symmetries results in the ground state being, as a rule, either a doublet with $J_z = \pm 1/2$ and $\mu_{eff} = 0.25\mu_B$ or a doublet with $J_z = \pm 5/2$ and $\mu_{eff} = 1.24\mu_B$. Our data suggest that the ground state in a field of symmetry C_s is most probably the first doublet, with a splitting of 10–11 K.

It was earlier found that the van Vleck susceptibility of Eu^{3+} ions in related compounds $La_{1-x}Eu_xCoO_3$ practically coincides with that of free ions [26]. The matter is that the ground state of Eu^{3+} is the singlet $^7F_0$, $J = 0$, which is not split by the crystal field. In our case the situation is radically different. Thus, the crystal field effect is very large.

5. CONCLUSIONS

Our experimental study of the static magnetization of $GdCoO_3$ and $SmCoO_3$ cobaltites has revealed that, below room temperature, the trivalent cobalt ions in these compounds reside predominantly in the nonmagnetic low-spin state. The magnetization originates primarily from the magnetic moments of the Gd^{3+} and Sm^{3+} rare-earth ions. The $GdCoO_3$ compound exhibits a weakly pronounced antiferromagnetism, possibly associated with oxygen nonstoichiometry, but deviations from the pure paramagnetic behavior are, on the whole, not very large. The effective moment of Gd^{3+} obtained in the experiment is lower than the theoretical value for the free ion by only 7%. Hence, in $GdCoO_3$, the magnetic system is an ensemble of weakly interacting Gd^{3+} ions, whose properties are close to those of free ions. This is far from being true for $SmCoO_3$, in which the experimental value of the orientational component of the Sm^{3+} magnetic moment is substantially lower than that characteristic of the free ion. Moreover, $SmCoO_3$ reveals a clearly pronounced van Vleck polarizational paramagnetism with a susceptibility considerably larger than that of the free ions. This strong difference between the low-temperature magnetic properties of two compounds with close compositions should be assigned to the difference in their electronic shell structures. The Gd^{3+} ion is an S ion with a zero orbital moment and a symmetric electronic shell. Therefore, the Gd^{3+} ground state is practically unaffected by the crystal field. By contrast, the ground state multiplet of Sm^{3+} is crystal-field split into three Kramers doublets. This brings about partial freezing of the orbital moment and the corresponding decrease in the orientational component of the magnetic susceptibility. At the same time, the van Vleck susceptibility component of Sm^{3+} ions in $SmCoO_3$ turns out to be larger than that of the free ion, which suggests a higher polarizability of the ion electronic shell in crystal field.

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