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Magnetic and Resonance Properties of $Bi_{24}(CoBi)O_{40}$

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Temperature and field dependences of the magnetic moment in the temperature range 4 K $< T <$ 300 K and electron spin resonance linewidths and the g-factor in the temperature range 80 K $< T <$ 300 K for the $Bi_{24}(CoBi)O_{40}$ compound synthesized by the solid-state reaction are analyzed. The magnetic susceptibility of $Bi_{24}(CoBi)O_{40}$ within the range 4 K $< T <$ 300 K is described well by the Curie-Weiss law with the negative paramagnetic Curie temperature $\theta = -12.3$ K and the effective magnetic moment $\mu = 5.08\mu_B$. The g-factor and the ESR linewidth grow with temperature.

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I. INTRODUCTION

As is known, mixed-valence compounds exhibit intriguing magnetic and electrical properties. Examples of such compounds are $La_{1-x}A_xMnO_3$ (A = Sr, Ca, or Ba) manganites [1,2] with orbital, spin, and charge ordering. The well-studied Fe_3O_4 iron oxides with the charge ordering in the magnetically ordered region are characterized by high conductivity caused, in particular, by closeness of divalent and trivalent iron ions in the octahedral positions [3,4]. The Co_3O_4 [5] and Mn_3O_4 [6] oxides are characterized by low conductivity, which is attributed to the difference in crystalline structures, since the main contribution to the kinetic properties is made by hoppings of electrons between cations in the tetrahedral and octahedral sites. The magnetic and electrical properties of these compounds with the charge ordering are determined by electrons of the 3d metals. The charge ordering can be formed by removal of orbital degeneracy of electrons in the 3d states due to the spin-orbit interaction and the interaction with phonon modes. The aim of this study was to establish the correlation between the magnetic and elastic characteristics of a semiconductor with the charge ordering.

II. EXPERIMENTS AND DISCUSSION

Polycrystalline bismuth cobaltite was synthesized by the solid-state reaction. According to the data of the X-ray analysis, the synthesized compound consists of two phases, $Bi_{24}(CoBi)O_{40}$ and Co_3O_4. The refinement of the structures, unit cell parameters, profiles of the diffraction peaks, and contents of the phases in the sample was performed with the DDM program [7]. The main $Bi_{24}(CoBi)O_{40}$ phase is characterized by cubic symmetry with the non-centrosymmetric space group I23 [8]. The lattice parameters are $a = 10.1917(1)$ Å for $Bi_{24}(CoBi)O_{40}$ and $a = 8.0842(1)$ Å for Co_3O_4. The Co_3O_4 phase has the normal spinel structure [5,9]. The contents of the $Bi_{24}(CoBi)O_{40}$ and Co_3O_4 phases in the sample are 77.0(5) and 23.0(5)%, respectively.

The differential thermal analysis curve has no anomalies up to the temperature $T = 1157$ K, which indicates the absence of phase transformations in the sample.

The magnetic properties of the sample were investigated on a MPMS XL facility (Quantum Design) in the temperature range 4 K $< T <$ 300 K at a sample heating rate of 4 K/min. Temperature dependences of the magnetic susceptibility of the two-phase $0.77Bi_{24}(CoBi)O_{40}\cdot 0.23Co_3O_4$ compound and the Co_3O_4 cobalt oxide measured in the magnetic field $H = 5$ are presented in Fig. 1. The magnetic susceptibility curve of cobalt oxide has the maximum in the tempera-

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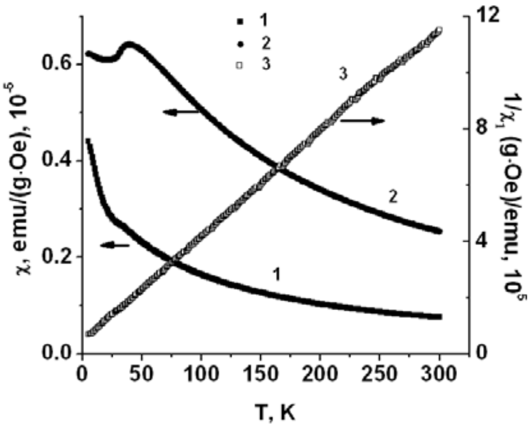

Fig. 1. Temperature dependences of magnetic susceptibility for (1) $0.77Bi_{24}(CoBi)O_{40}\cdot 0.23Co_3O_4$ and (2) Co_3O_4 and (3) temperature dependence of the inverse magnetic susceptibility for the one-phase $Bi_{24}(CoBi)O_{40}$ sample (H = 5 T).

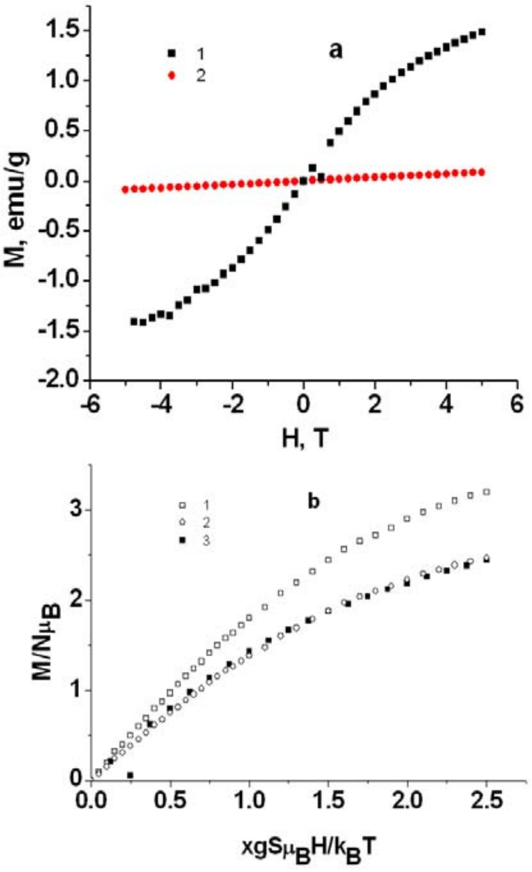

Fig. 2. (Color online) (a) Magnetization curves $M(H)$ $Bi_{24}(CoBi)O_{40}$ at (1) T = 5 K and (2) T = 300 K. (b) Brillouin function $M/N\mu_B = gSBS(gS\mu_B H/k_B T)$ for the contents of paramagnetic atoms (1) $x = 1$ and (2) $x = 0.78$ versus magnetic field normalized on the temperature T = 5 K and (3) the experimental data for $Bi_{24}(CoBi)O_{40}$ (3).

ture region near $T_{max} = 39$ K; the maximum derivative $d\chi/dT$ is observed at $T = 32$ K. Magnetic susceptibility χ_1 of the $Bi_{24}(CoBi)O_{40}$ phase was found by subtracting magnetic susceptibility χ_2 of cobalt oxide with allowance for the weight ratio from the susceptibility of the two-phase sample: $\chi_1 = \chi - 0.23\chi_2$. Figure 1 shows the temperature dependence of the inverse susceptibility $1/\chi_1$ for the $Bi_{24}(CoBi)O_{40}$ phase in the temperature range 4 K $< T <$ 300 K. This dependence is described well by the Curie-Weiss law with the negative paramagnetic Curie temperature $\theta = -12.3$ K and the effective magnetic moment $\mu = 5.08\ \mu_B$. Based on these data, we assume that the magnetic moment of the $Bi_{24}(CoBi)O_{40}$ phase is caused by spins of trivalent cobalt ions located in the tetrahedral positions with $S = 2$. The absence of the long-range magnetic order for $Bi_{24}(CoBi)O_{40}$ at $T > 4$ K is possibly related to the spin-phonon interaction, which decreases the Neel temperature and, at a certain critical interaction parameter, eliminates the long-range magnetic order. Only the short-range order remains, which also yields a finite value of the paramagnetic Neel temperature. To determination the effect of an external magnetic fields, we measured the magnetization in the fields –5 T $< H <$ 5 at the temperatures $T = 5$ K and $T = 300$ K. The magnetization of the $Bi_{24}(CoBi)O_{40}$ phase was determined by the subtraction: $M[Bi_{24}(CoBi)O_{40}] = M[0.77Bi_{24}(CoBi)O_{40}\cdot 0.23Co_3O_4]$ - $M[0.23Co_3O_4]$. Figure 2(a) shows field dependences of magnetization at the temperatures $T = 5$ K and $T = 300$ K. At $T = 5$ K, the compound under study is in the paramagnetic state and the magnetization is described by the Brillouin function $M/N\mu_B = gSB_S(gS\mu_B H/k_B T)$, where $x = 1$ and 0.78 (see Fig. 2(b) for the cobalt ion spin $S = 2$). The discrepancy between the theoretical and experimental results is due to action of the magnetic field of the Co_3O_4. Clusters and nanowires of Co_3O_4 reveal residual magnetic moment. The magnetization arising from the uncompensated spins is calculated as ~ 0.02 emu/g [10]. Magnetic field created by the surface Co^{3+} cations induces the small ferromagnetic ordering into the $Bi_{24}(CoBi)O_{40}$, that may be interpreted as decreasing of volume part of the $Bi_{24}(CoBi)O_{40}$ compound in paramagnetic state. The fraction of the paramagnetic phase is $x = 0.78$, which is determined by fitting the Brillouin function $M^{ex}/\mu_B = gSBS(gSH\mu_B/k_B T)$ to the experimental data (Fig. 2(b)).

The interaction between the spin and elastic subsystems is revealed by electron spin resonance (ESR). In both compounds, a magnetic cobalt ion is in the tetrahedral surrounding. Crystalline fields into $Bi_{24}(CoBi)O_{40}$ and into Co_3O_4 on cobalt ions in the tetrahedrons slightly differ and it leads to two resonance fields, one of which will agree with the results Co_3O_4 [9]. The shape of the ESR line is somewhat asymmetrical, since the half-linewidths $\Delta H_1/2$ and $\Delta H_2/2$ on the right and on the left from the resonance differ by 10 Oe. This difference is within one percent of the linewidth and caused by closeness of the resonances from cobalt spins in Co_3O_4 and $Bi_{24}(CoBi)O_{40}$, whose g-factors also differ by about one percent. Temperature dependences of the g-factor and

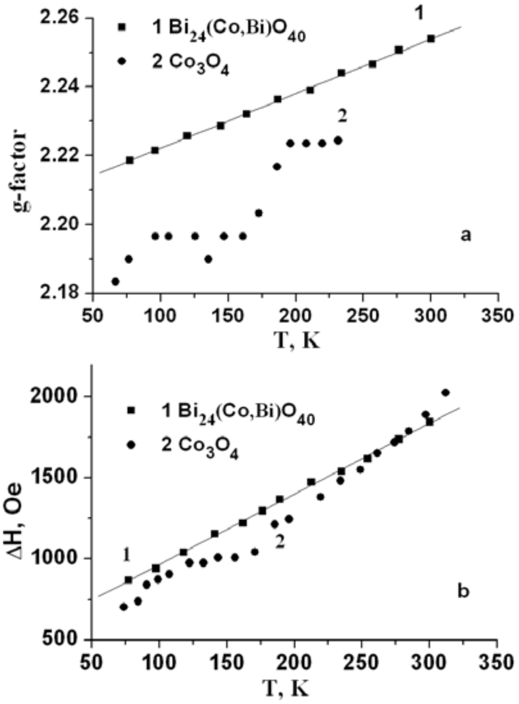

Fig. 3. Temperature dependence of (a) the g-factor and (b) the ESR linewidth for (1) $Bi_{24}(CoBi)O_{40}$ and (2) Co_3O_4 [9].

the ESR linewidths for the two-phase sample and cobalt oxide are presented in Fig. 3. The experiment shows that upon heating the resonance field decreases and the g-factor grows from 2.22 to 2.25. The growth of the g-factor in Co_3O_4 is still unexplained; in $Bi_{24}(CoBi)O_{40}$, it is possibly caused by local structural distortions at varying bismuth valence, which lowers local symmetry. The ESR linewidths in the two compounds coincide accurate to 16%. They linearly grow with temperature, which indicates the interaction between spins and phonons. Linewidth ΔH for the polycrystalline sample is described by the equation $\Delta H = C/T\chi[K(T)] + f(\varepsilon)$ [9], where C is the Curie constant, $K(T)$ is the secondary term that reflect the spin-phonon interaction, and $f(\varepsilon)$ is the critical contribution near the Neel temperature. At $T >> \theta$, the temperature dependences of ΔH and $K(T)$ coincide. Relaxation of spin moments is implemented via the elastic subsystem. A trivalent cobalt ion belongs to Jahn-Teller ions and orbital degeneracy can be eliminated by the dynamic interaction with the tetrahedron oscillation modes.

III. CONCLUSIONS

The magnetic properties of the $Bi_{24}(CoBi)O_{40}$ compound containing bismuth ions Bi^{5+} and Bi^{3+} with an occupied and unoccupied 6*s* shell are determined by cobalt ions with the weak antiferromagnetic interaction. In the paramagnetic state, the strong spin-phonon interaction has been found that leads to the growth of the ESR linewidth.

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