SEMICONDUCTORS
AND DIELECTRICS

Magnetic and Electrical Properties
of Cobalt Oxyborate Co₃BO₅

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Abstract—Single crystals of cobalt oxyborate Co_3BO_5 are synthesized. The results of investigations into the structural, magnetic, and electrical properties are reported. It is found that Co_3BO_5 crystals exhibit two magnetic anomalies at $T_1 = 17$ K and $T_2 = 45$ K. The temperature dependence of the electrical resistivity is investigated. Deviations both from the activation law of variation in the electrical resistance and from the Mott variable-range hopping conduction are revealed.

1. INTRODUCTION

Homometallic and heterometallic oxyborates with one or several transition-metal ions have been intensively investigated both experimentally and theoretically. These materials crystallize in structures of calcite, warwickite, ludwigite, huntite, and norbergite, which names are taken from their isostructural minerals [1, 2]. Transition-metal oxyborates have attracted considerable research attention owing to the rich variety of their magnetic, electrical, and optical properties. The low dimension combined with a random distribution of cations over nonequivalent crystallographic positions accounts for the existence of a number of structural, magnetic, and electronic phase transitions [3].

The general formula of oxyborates with a ludwigite crystal structure (space group *Pbam*) can be written as $M_2M'(BO_3)O_2$, where M^{2+} = Ni, Mg, Fe, or Cu and M'^{3+} = Co, Cr, V, Fe, or Mn [4–6]. The unit cell of these compounds contains four formula units. In the ludwigite crystal lattice, the transition metal has an oxygen environment and can be located in four nonequivalent positions occupied by divalent and trivalent ions. The oxygen edge-shared octahedra form zigzag walls consisting of octahedral ribbons. The ratio of the metal to boron for ludwigites is 3 : 1. The octahedral ribbons are responsible for the low-dimensional magnetic and electronic properties of the ludwigites. Within a ribbon, there can occur both an indirect *M*–O–*M* exchange and a direct exchange. The weak bounding between ribbons determines the quasi-one-dimensional character of the magnetic structure, which makes the ludwigites a suitable object for comparison with the theoretical concepts of Heisenberg antiferromagnetic chains.

Among the oxyborates with a ludwigite structure, the best studied are the heterometallic compounds with unlike metals acting as divalent and trivalent ions, for example, Mg^{2+} and Mn^{3+} [7] or Mg^{2+} and Al^{3+} [8]. Norrestam et al. [7] were the first to synthesize a homometallic compound with a ludwigite structure, namely, Co_3BO_5, in which nonequivalent crystallographic positions are occupied by like metal ions in different valence states. Moreover, those authors performed structural investigations proving that this compound belongs to space group *Pbam*, calculated the Co–O valence bond lengths for different positions of the cobalt ion, and estimated the probabilities of divalent and trivalent ions occupying a lattice position [7]. Although more than fifteen years have elapsed since the publication of that paper, the physical properties of the Co_3BO_5 compound have remained completely unknown. This may be ascribed to the fact that the single crystals grown in those times were very small (about $0.018 \times 0.023 \times 0.100$ mm in size [7]), which greatly complicated investigation of their magnetic and electrical properties. The present paper will attempt to fill in this gap.

2. EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

Our single crystals, grown by the melt solution technique, were thin needles of black color characteristic of ludwigites [6, 7]. The needles were up to 2 mm long. The cross section of a needle is presented in Fig. 1. Arrows *1* and *2* specify the directions of the magnetic field applied in the magnetic measurements.
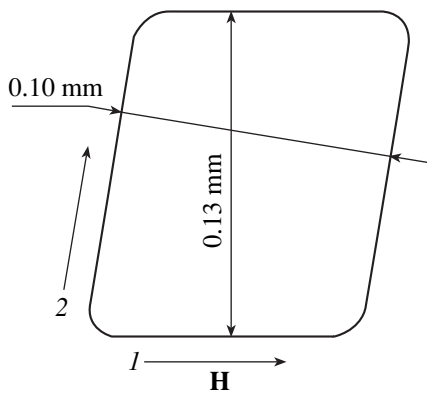
Fig. 1. Cross section of the crystal.

Fig. 2. Temperature dependences of the magnetization in (a) the magnetic field applied in direction *1* (Fig. 1) at $H =$ (*1*) 100, (*2*) 200, (*3*) 400, and (*4*) 600 Oe and (b) the magnetic field applied in direction *2* (Fig. 1) at $H =$ (*1*) 200 and (*2*) 400 Oe.

The table presents our x-ray diffraction data on the unit cell parameters for Co_3BO_5 in comparison with the data reported in [7]. Our unit cell parameters are seen to differ slightly from those in [7]. The density of the samples is 5 g/cm^3.

The Co_3BO_5 samples were found to be paramagnetic at room temperature. The temperature dependences of the magnetization M measured on a SQUID magnetometer in different external static magnetic fields (up to 600 Oe) applied in direction *1* (Fig. 1) and in direction *2* (Fig. 1) are shown in Figs. 2a and 2b, respectively. Open symbols correspond to measurements in a zero-field cooling (ZFC) mode, and filled symbols are experimental data obtained in a field cooling (FC) mode in magnetic fields H. All the curves were measured under heating of the samples.

The dependences $M(T)$ measured in different directions of the magnetic field are similar to each other and exhibit two magnetic anomalies: the first anomaly is observed at $T_1 \sim 17$ K, and the second anomaly, at $T_2 \sim$ 45 K. It can be seen from Fig. 2 that the magnetization drastically increases at 45 K for both orientations of the magnetic field, whereas the anomaly observed at 17 K for field direction *1* (Fig. 1) is smeared. In the magnetic field aligned with the needle, the magnetization is close to zero, which suggests an easy-plane anisotropy.

The temperature dependence of the electrical conductivity σ in semiconductor materials frequently obeys the law

$$\sigma = \sigma_0 \exp(-\Delta/kT^{1/n}).$$

Here, σ_0 and Δ are constants related to the band structure parameters and n is an integer. For $n = 1$, the conductivity follows the simple activation law characteristic of wide-band-gap intrinsic and extrinsic semiconductors, with the constant Δ corresponding to the activation energy of conduction. The value $n = 2$ implies the existence of strong electronic correlations, which give rise, as was shown in [9], to a Coulomb gap in the spectrum of electronic states. The case $n = 4$ corresponds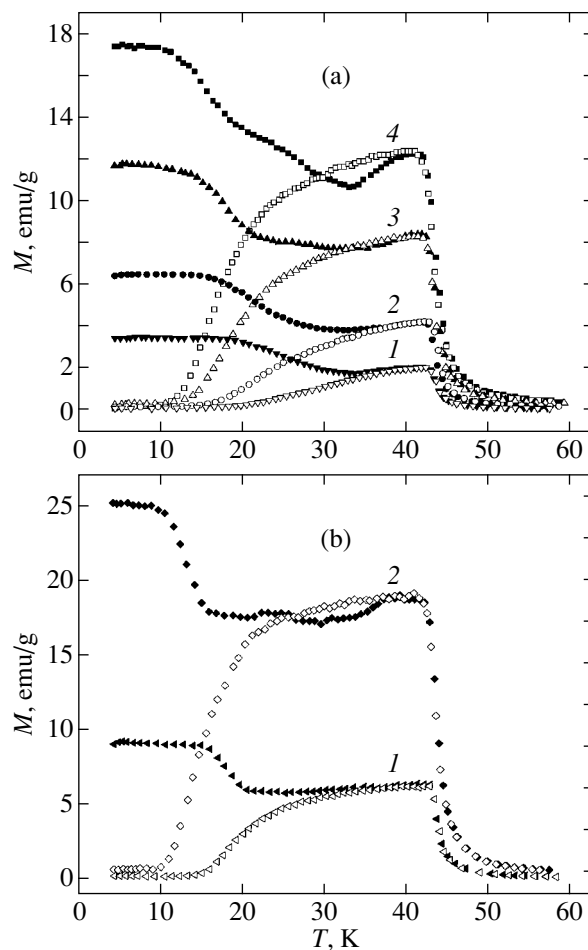 to the Anderson localization of charge carriers and the Mott law of variable-range hopping conduction. The conduction obeying laws with $1 \leq n \leq 4$ has been repeatedly observed experimentally and widely described in the literature [10, 11]. A change in the temperature leads, in some cases, to a conversion from one behavior of the conductivity to another. The phase diagrams calculated in [12] show that the range of applicability of the Mott law is bounded from above and from below both in carrier concentration and in temperature. The conversion from the simple activation law to the Mott law of variable-range hopping conduction with decreasing temperature was observed in our earlier work [13] for the $Fe_{1-x}V_xBO_4$ warwickite, which is related to the compound described in the present publication.

The temperature dependences of the electrical conductivity σ of Co_3BO_5 samples are presented in Fig. 3 on a semilogarithmic scale. The quantity proportional to the inverse temperature $1/T$ is plotted along the abscissa axis in Fig. 3a, and that proportional to the
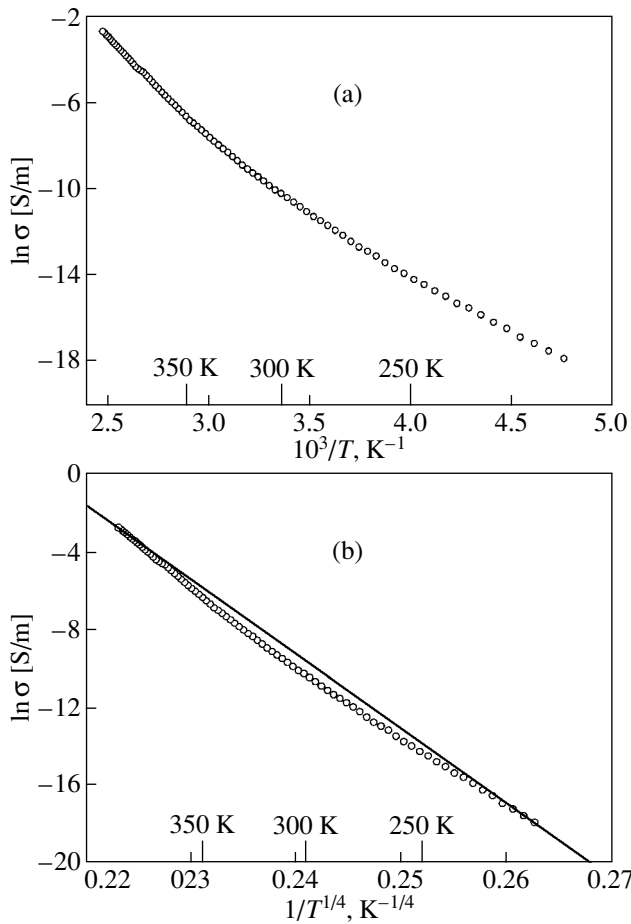
Fig. 3. Dependences of the logarithm of the electrical conductivity on (a) the inverse temperature and (b) the temperature to the –1/4 power.

temperature to the –1/4 power, in Fig. 3b. For the simple activation law

$$\sigma = \sigma_{01} \exp(-\Delta_1/kT),$$

the former dependence should be linear. In the case of the Mott law of variable-range hopping conduction,

$$\sigma = \sigma_{02} \exp(-\Delta_2/kT^{1/4}),$$

the latter dependence (shown in Fig. 3b) should be linear. It can be seen from Fig. 3 that both dependences are substantially nonlinear. Therefore, the kinetic phenomena observed for Co_3BO_5 cannot be described by invoking only one of the above mechanisms of carrier trans-

fer. It seems likely that the temperature range covered is a transition region in which the conduction mechanisms changes. As can be seen from Fig. 3a, the logarithmic curve of the conductivity transforms in the high-temperature range into a straight line, which apparently corresponds to an activation law with $n = 1$. In the low-temperature range, the sample becomes dielectric, which suggests carrier localization.

3. CONCLUSIONS

Thus, we synthesized single-crystal cobalt oxyborate Co_3BO_5. It was shown that, at temperatures below 45 K, the compound is magnetically ordered. A magnetic anisotropy of the easy-plane type was revealed. The transport properties of the Co_3BO_5 oxyborate suggest that this compound can be classed among Mott–Hubbard insulators. The conversion to the activation law of conduction takes place in the range close to room temperature.

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Unit cell parameters of the Co_3BO_5 single crystals

Parameter	[7]	This study
a, Å	9.275	9.302
b, Å	12.146	11.957
c, Å	3.0265	2.972
V, Å^3	340.95	330.58