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Magnetic Properties of $EuBaCo_2O_{5.5}$ Single Crystals

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The static magnetization of the $EuBaCo_2O_{5.5}$ single crystals was measured from helium to room temperatures for two configurations of the applied field: parallel and perpendicular to the c-axis. The compound is antiferromagnetic from helium temperature to about 210 K. In low temperature region (below 45 K) the antiferromagnetism coexists with a spin-glass-like state. The metamagnetic field-induced phase transition was observed in the antiferromagnetic phase for magnetic field applied perpendicular to the c-axis. The spontaneous phase transition from antiferromagnetic to weak ferromagnetic phase was established to be of the first order. This transition is accompanied by the appearance of the intermediate state. The weak ferromagnetic phase exists up to $T_c = 240$ K.

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1. Introduction

The layered rare-earth cobaltites $LnBaCo_2O_{5+x}$ (Ln — rare earth) are of great interest since they show charge order, metal–insulator and many other magnetic transitions depending on a kind of lanthanide and the oxygen content x [1]. In the case of $EuBaCo_2O_{5+x}$ Martin et al. [1] reported that for $x = 0.4$ a metal–insulator transition takes place at 360 K accompanied by the paramagnetic to ferromagnetic phase transition at 270 K. It was also shown that below 260 K the system displays a phase transition to an antiferromagnetic phase.

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In this paper we are going to present detailed studies of the magnetic properties of $EuBaCo_2O_{5.5}$ performed for the first time on single crystals.

2. Experimental

Single crystals were grown by a spontaneous crystallization from over stoichiometric flux melt [2]. The as grown crystals are of the tetragonal symmetry ($P4/mmm$ space group). The crystals were next annealed for 20 h at 600°C at oxygen atmosphere, under the pressure of 3 at, and then cooled at a rate of 10°C/h down to room temperature. The powder X-ray diffraction of annealed samples showed a single phase of the orthorhombic structure without any traces of other phases. The value of x was estimated to be 0.5 (± 0.02).

The magnetization measurements $M(H,T)$ were performed using SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 2–350 K at magnetic fields up to 50 kOe.

3. Results and discussion

The temperature variation of the magnetization of a single crystal of $EuBaCo_2O_{5.5}$ measured at 100 Oe in three different thermo-magnetic regimes is presented in Fig. 1. Beside the measurements in the regime of zero field cooling (ZFC), measurements during field cooling (FCC) and next on warming (FCW) have been shown. The external magnetic field in these measurements was applied perpendicularly to the c-axis. Since the crystal is twinned with twinning boundaries intersecting the ab plane, we have neglected any angular dependences of magnetization in the ab plane. As is seen from Fig. 1 the ZFC magnetization increases rapidly near $T_c = 240$ K reaching the maximum near $T_{\max} = 220$ K. The magnetic moment per Co ion at $T_{\max}$ is about 0.04 μ_B/Co for $H = 100$ Oe. For $H = 1$ kOe, which is close to the saturation field, the magnetic moment is only about 0.1 μ_B/Co which suggests weak ferromagnetic ordering (WFM) of Co^{3+} ions (or more generally, noncollinear antiferromagnetic ordering). Below $T_{\max}$ the magnetic moment of the system sharply decreases and the system transfers into the antiferromagnetic state (AFM) at temperature $T_N = 210$ K. Below T_N one can remark in Fig. 1 the following features of observed $M(T)$ dependences:

(i) the most striking is the distinct difference between ZFC magnetization (M_{ZFC}) and both M_{FC} (M_{FCC} and M_{FCW}) ones in whole temperature range $T < T_N$. Such situation is unusual for antiferromagnets. In order to explain such behavior of the crystal one should assume that the difference between ZFC and FCC (FCW) magnetization could arise as an effect of induced ferromagnetic order near various defects (including twinning walls) in the process of sample cooling or warming in an external magnetic field. It means that the system is magnetically inhomogeneous with ferromagnetic regions embedded into antiferromagnetic matrix.

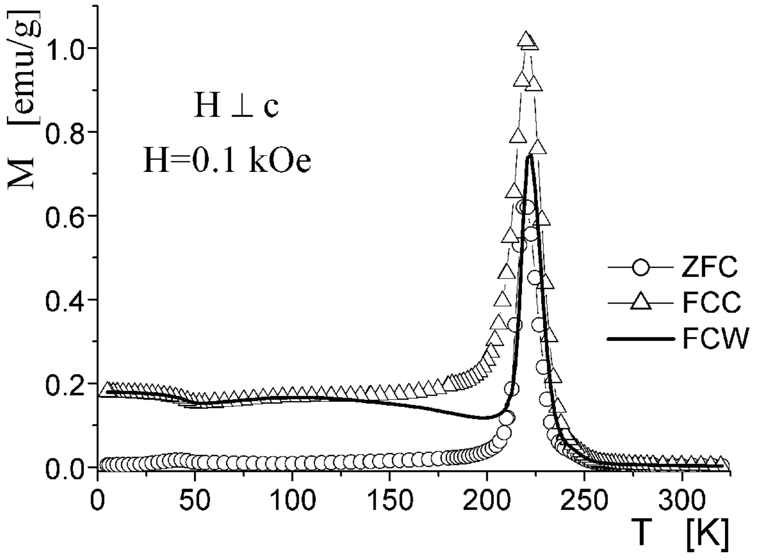

Fig. 1. The dc susceptibility $\chi(T)$ in $H = 100$ Oe for $H \parallel [100]$ for three regimes: zero field cooling (ZFC, ○), field cooling with measurements on cooling (FCC, Δ) and on warming (FCW, full line).

(ii) at 120 K the difference between M_{FCC} and M_{FCW} appears and is observed at least up to $T_{\max}$. This difference seems to be due to an intermediate state arising because of the first-order character of the phase transition AFM–WFM.

(iii) below $T_{\mathrm{f}} \approx 45$ K an additional mechanism seems to appear, which gives a contribution to the difference between M_{ZFC} and M_{FC} (M_{FCC} and M_{FCW}). This contribution suggests the presence of disordered spins frozen in a spin-glass-like state at low temperatures. A detectable increase in the FC magnetization below T_{f} and a peak at T_{f} in the ZFC magnetization may originate from the Eu^{3+} magnetic moments interacting with Co^{3+} moments. This interaction could result in the frustration of long-range magnetic ordering [3]. It should be stressed that below T_{f} (for ZFC regime) the dominating AFM phase coexists with mentioned above spin-glass phase.

Figure 2 presents magnetization curves at 5 K ($T < T_{\mathrm{f}}$) measured in the magnetic field applied perpendicular and along the c-axis. One can see that the ab plane is an easy plane or that the easy axis is situated in this plane. A narrow hysteresis displayed in Fig. 2 for $H \parallel c$ seems to be due to a small disorientation of the c-axis in relation to the magnetic field direction.

The character of the initial magnetization curves (Fig. 3) confirms once more that AFM order exists in the studied system even at the lowest temperature (in our case it was 5 K) below T_{f}. It is seen that the initial magnetization curve at 5 K displays a metamagnetic type transition. Since this transition is induced by

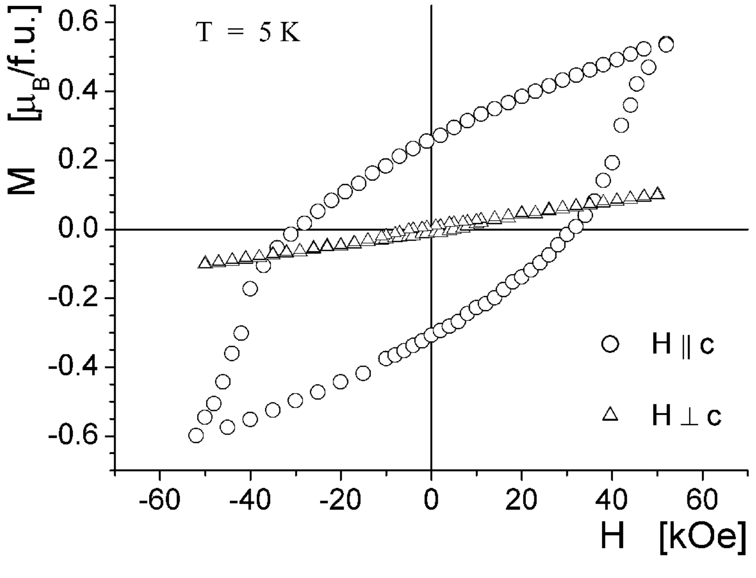

Fig. 2. Hysteresis loops measured at 5 K for two orientations $H \parallel c$ (○) and $H \perp c$ (△).

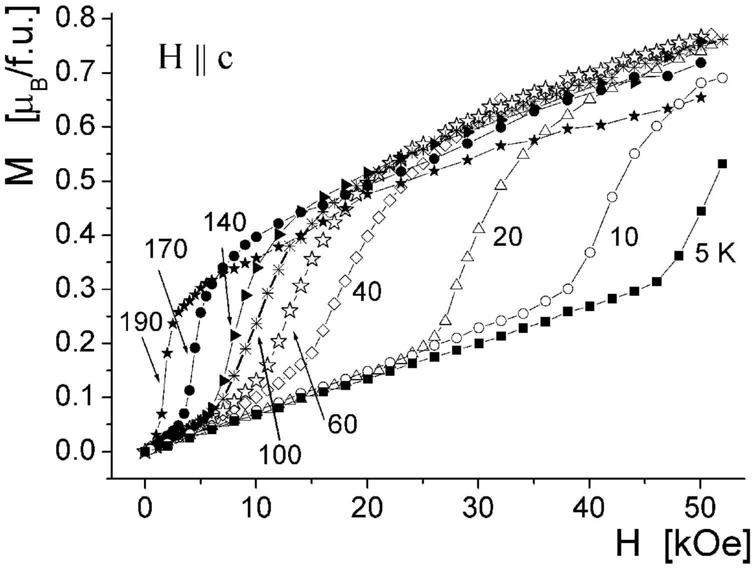

Fig. 3. Initial magnetization curves for various temperatures below T_N. Magnetic field was applied parallel to the c-axis.

magnetic field applied in the *ab* plane one can conclude that AFM vector (and easy direction of magnetization of Co^{3+} subsystem) is located in this plane. The value of the transition field decreases from about 50 kOe at 5 K to about 5 kOe near 100 K. For highly anisotropic system the transition field is determined [4] for $T = 0$ by

$$H_{\mathrm{tr}} = \mu|\lambda_{12}|,$$

where μ is the magnetic moment of Co^{3+} ion, λ_{12} is the molecular field coefficient describing the exchange field between nearest neighbors.

Above 120 K (±10 K) the character of magnetization curves changes considerably (Figs. 3, 4). It should be related to the fact that in this temperature region up to T_{N} the system is in intermediate state. The hysteresis loops arise due to the phase domains existing near T_{N}. Generally, one should expect that the intermediate state consists of three types of phase domains (AFM phase, WFM phases with magnetization up and magnetization down). With increase in magnetic field, first the domains with WFM magnetization down are suppressed and then the domains consisting of antiferromagnetic phase should be suppressed. This unusual magnetization process is responsible for the rather strange shape of hysteresis loop. Small values of remanence observed for loops measured in the temperature range $120\ \mathrm{K} < T < T_{\mathrm{N}}$ is due to presence of all three phases mentioned above near $H \approx 0$. It gives characteristic low field narrowing of hysteresis curves (see as an example the hysteresis at 140 K in Fig. 4).

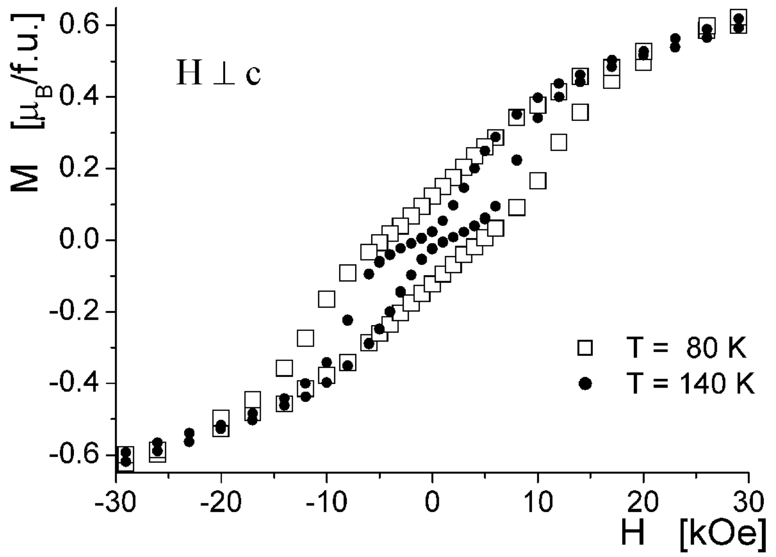

Fig. 4. Comparison of hysteresis loops for temperatures below and above 120 K ($H \perp c$).

In conclusion, it was shown that magnetic properties of the $\mathrm{EuBaCo_2O_{5.5}}$ single crystals are determined first of all by antiferromagnetic exchange interactions. Similar to other rare-earth layered cobaltites the studied crystals display a number of various phase transitions, particularly the transition from antiferromagnetic to weak ferromagnetic state. The coexistence of the antiferromagnetic long-range-order and spin-glass-like phase is a feature characteristic of the $EuBaCo_2O_{5.5}$ single crystals and not observed until now in other members of this family of cobaltites.

Acknowledgments

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