Anomalous magneto-crystalline anisotropy of MnCr2S4 single crystals

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Anomalous magneto-crystalline anisotropy of $MnCr_2S_4$ single crystals

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1. Introduction

The ternary ferrimagnet $MnCr_2S_4$ belongs to the family of magnetic chalcogenide semiconductors AB_2X_4 (A = Cd, Hg, Cu, Fe, Mn, Co; X = S, Se), in which magnetic and charge-transport properties are correlated [1,2]. Some of the compounds show half-metallic ferromagnetic behaviour [3, 4] and colossal magnetoresistance (CMR) similar to manganese oxide perovskites [5]. However, the origin of the CMR effect seems to be quite different for these two groups of magnetic materials [6]. The study of the magnetic properties of $MnCr_2S_4$ polycrystals yielded inconsistent results and left many open questions with respect to its magnetic structure [7–11]. The discrepancies in the previous data can probably be attributed to insufficient quality of the samples used. To shed light on the intrinsic properties of $MnCr_2S_4$ we present here the results of electron-spin-resonance (ESR) studies on $MnCr_2S_4$ single crystals. To our knowledge, this is the first communication on the magnetic properties of single crystals of this compound.

2. Experimental

$MnCr_2S_4$ single crystals were grown by the chemical transport reaction method [12] from the ternary polycrystalline material prepared by solid state reactions. Chromium chlorine was used as a source of the transport agent. X-ray diffraction analysis confirmed the single-phase cubic spinel structure of the samples with a lattice parameter of 10.112(4) Å in agreement with previous results on $MnCr_2S_4$ polycrystals [2]. Magnetization measurements were performed in the temperature range 2–300 K using Quantum Design MPMS-7 and MPMS-5 SQUID magnetometers. Utilizing a rotating sample holder permits to

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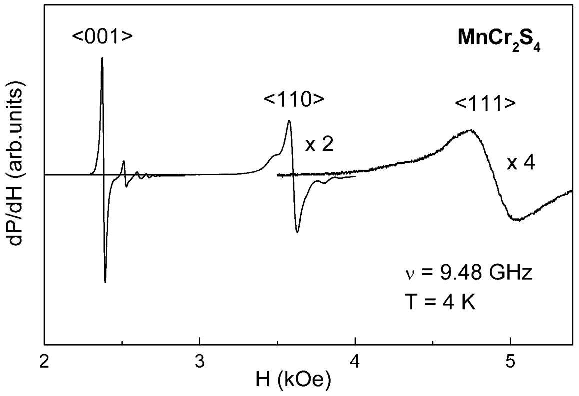

Fig. 1. ESR spectra for a MnCr$_2$S$_4$ single crystal (disk I) at 4 K for the magnetic field applied within the (110) plane along the three principal cubic axes.

investigate the angular dependence of the magnetization. ESR studies were performed in a CW X-band spectrometer (Bruker ELEXSYS E500) working at 9.48 GHz. The samples were cooled using a continuous He gas-flow cryostat (Oxford Instruments). The stability of temperature in the range $4.2 < T < 300$ K was ~0.1 K below 15 K and ~0.3 K for higher temperatures. The single crystals were shaped into polished thin disks with their surface parallel to the crystallographic (110) and (001) planes. The magnetic field was applied parallel and perpendicular to the surface. The orientation of the single crystalline samples in the principal directions was better than ±2°.

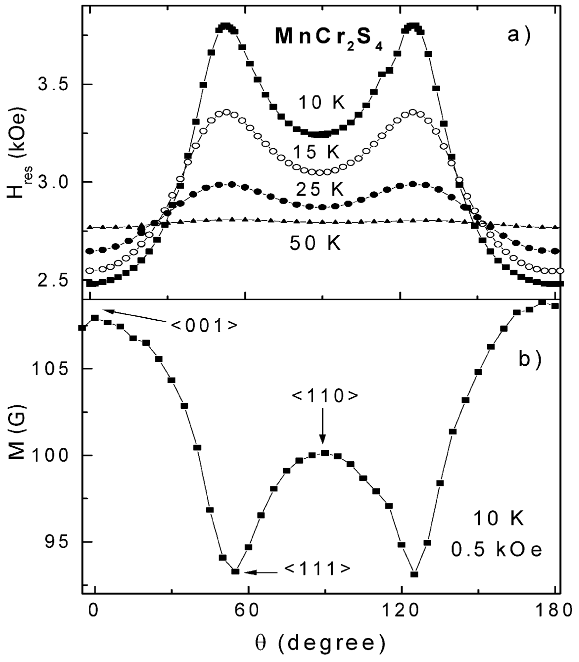

Fig. 2. (a) Angular dependence of the resonance field, H_{res}, for a single crystalline MnCr$_2$S$_4$ sample (disk II) at different temperatures for the magnetic field applied within the plane of the disk. (b) Angular dependence of the magnetization in a field of 500 Oe at 10 K for the same sample. Solid lines are guides to the eye.

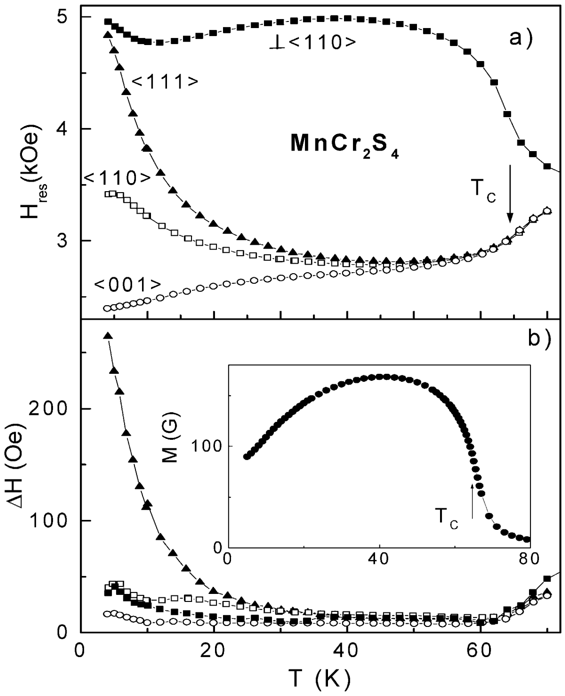

Fig. 3. Temperature dependences of the resonance field H_{res} (a) and the resonance linewidth ΔH (b), of a MnCr$_2$S$_4$ single crystal (disk I) for three principal crystal axes for in-plane and perpendicular configurations. Inset: temperature dependence of the magnetization in a field of 2 kOe for the easy direction.

3. Experimental results

Fig. 1 presents the ESR spectra at 4 K for one of the disk-like samples with the external magnetic field within the (110) plane along the three main crystallographic directions. Along the ⟨001⟩ axis a rather narrow resonance line is observed, whereas for the ⟨110⟩ and ⟨111⟩ axes the ESR line exhibits a larger linewidth. In addition to the main resonance, a series of weaker resonance lines were observed. They are generated by the excitation of magnetostatic modes [13]. We were able to reduce the number and intensity of these extra modes by an accurate preparation of the shape and surface of the samples and, thus, to identify the uniform precession mode.

The angular dependence of the resonance field, H_{res}, is shown in Fig. 2(a) for some temperatures below the Curie temperature ($T_C = 64.5$ K). The resonance field exhibits a maximum for the ⟨111⟩ and minima for the ⟨001⟩ and ⟨110⟩ directions, respectively. This behaviour is characteristic for a positive cubic magnetocrystalline anisotropy [13]. Fig. 2(b) presents the angular dependence of the magnetization measured below the saturation value on the same sample. As

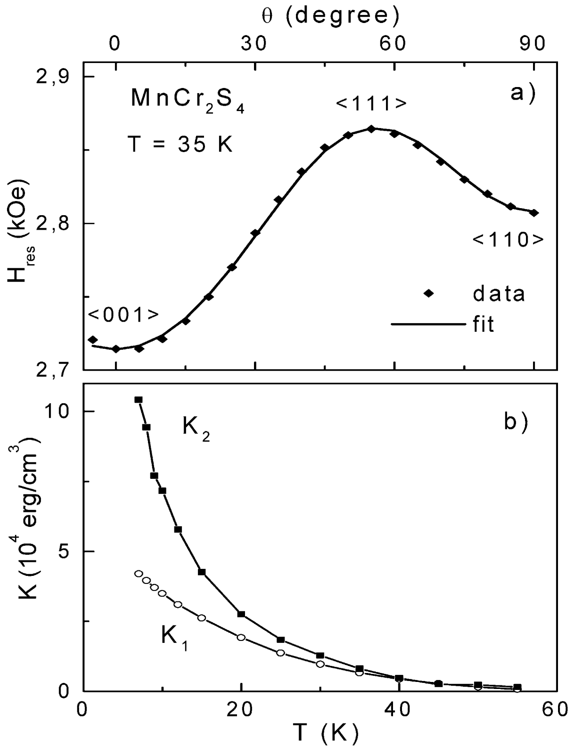

Fig. 4. Angular dependence of the resonance field H_{res} at $T = 35$ K with fitted curve (a) and temperature dependences of the first K_1 and second K_2 anisotropy constants (b) calculated from the ESR data of Fig. 3(a). Solid line in (b) is guide to the eye.

expected, the easy direction of magnetization lies along the ⟨001⟩ axis, whereas the ⟨110⟩ and ⟨111⟩ directions correspond to the intermediate and hard axes, respectively. The resonance linewidth (not presented here) also shows a pronounced angular dependence with extrema for the same directions as exhibited by the resonance field.

In Fig. 3(a) the temperature dependence of the resonance field is presented for the field within and perpendicular to the (110) plane. The temperature evolution of the resonance field can be described well by the Kittel formula [15]. In the temperature range $42 < T < 70$ K the value of the in-plane resonance field decreases for all the three directions. This may be interpreted as caused by an increase of the magnetization with decreasing temperature after the onset of magnetic order. The contribution to H_{res} of the demagnetizing field, which is proportional to the magnetization M, seems to exceed that of the anisotropy field in this temperature range. Below 42 K the resonance line for the easy magnetization direction ⟨001⟩ still shifts towards lower fields, whereas for the hard and intermediate magnetization directions an increase of H_{res} is observed. This behaviour may be explained by a strong increase of the anisotropy field which overcompensates the effect of the decrease of the demagnetizing field on H_{res}. The decrease of the demagnetizing field reflects the decrease of the magnetization, which exhibits a maximum at around 42 K (see inset in Fig. 3(b)). In contrast to the case of a field along the easy axis, for the magnetic field along the hard and intermediate directions of magnetization the demagnetizing and anisotropy fields enter with opposite sign in the Kittel formula [14,15]. Therefore, the observed increase of H_{res} indicates a much stronger increase of the anisotropy field compared to the decrease of the demagnetizing field below 42 K. For the magnetic field perpendicular to the (110) plane a similar competition of the anisotropy and demagnetizing fields may explain the observed non-monotonic temperature behaviour of H_{res} at temperatures below 42 K.

The resonance linewidth, ΔH, also exhibits a complicated behaviour with temperature (Fig. 3(b)). In the paramagnetic region (not shown here) ΔH is isotropic. It has a value ~150 Oe at 300 K and decreases by an order of magnitude approaching the Curie temperature. In the temperature range $60 > T > 40$ K, ΔH is nearly independent of temperature for the external magnetic field both within and perpendicular to the (110) plane. With the field applied along the easy axis it reaches a minimal value, ΔH_{min}, of about 8 Oe. The value of ΔH_{min} varies between 5 and 9 Oe for different samples. This variation is probably due to deviations from the ideal stoichiometry dependent on the growth conditions. Larger values of ΔH_{min} were observed for the samples prepared at higher temperatures. Below 40 K the linewidth increases slightly (~2 times) down to 4 K for the field along the easy axis of magnetization, ⟨001⟩, whereas it increases by about of factor of 5 for the field along the intermediate direction ⟨110⟩. For the hard magnetization direction, ⟨111⟩, the linewidth ΔH increases sharply below 15 K, reaching a value of about 300 Oe at 4 K.

We fitted the angular dependences of the resonance fields and calculated the values of the anisotropy constants using the expressions for the resonance conditions in a thin disk [15] and taking into account the effective demagnetizing factors of the magnetic anisotropy [16,17] as well as the values of shape demagnetizing factors, $N_\perp$ and $N_\parallel$, determined from the magnetization measurements. The results of such a fit to the angular dependence of H_{res} at a selected temperature are presented in Fig. 4(a) and (b) shows the temperature dependences of the first, K_1, and the second, K_2, anisotropy constants. We note that to describe the angular dependence shown in Fig. 4(a), both K_1 and K_2 have to be taken into account. As seen from Fig. 4(b), K_2 is even higher than K_1. Both, K_1 and K_2, exhibit a monotonic increase with decreasing temperature. The ratio K_2/K_1 has a minimum at $T \sim 42$ K. At temperatures below 42 K this ratio increases strongly until the value of K_2 is nearly two times larger than K_1 for $T = 7$ K. Below 7 K a second resonance line appears, which distorts the shape of the main line and prevents a reliable calculation of K_1 and K_2.

4. Discussion

The large difference (~2500 Oe) observed between the values of the resonance fields for ⟨001⟩ and ⟨111⟩ directions at 4 K (see Figs. 1 and 3) is rather surprising for $MnCr_2S_4$. Recent X-ray photoelectron-spectroscopy (XPS) investigations of our single crystals suggest that Cr and Mn ions are in the $3d^3$ (Cr^{3+}) and $3d^5$ (Mn^{2+}) state, respectively [17]. As it is well known, the orbital momentum of the free Cr^{3+} ion $^4F_{3/2}$ ground state is quenched in a cubic crystal field [18]. Calculations have shown that the anisotropic contribution of the purely octahedrally co-ordinated Cr^{3+} ions should be small (~10^3 erg/cm^3) [19]. Experimentally obtained values of K_1 for the related $CdCr_2X_4$ (X = S, Se) single crystals vary between 1 and 4×10^3 erg/cm^3 and agree well with these calculations [20–23]. On the other hand, the ground state $^6S_{5/2}$ of a Mn^{2+} ion in a cubic crystal field is an orbital singlet (configuration with zero orbital momentum) and, therefore, the contribution of the Mn^{2+} ions to the anisotropy is also expected to be small [18].

The origin of the strong magnetocrystalline anisotropy found by us in the $MnCr_2S_4$ single crystals is not clear at the moment. We note that the character of this anisotropy is similar to one observed in the related compounds $FeCr_2S_4$ and $CoCr_2S_4$ [24–26], where it appears to be due to the strong spin-orbit coupling typical for tetrahedral $3d^6$ Fe and $3d^7$ Co ions [20,27]. Similar results were obtained for $CdCr_2X_4$ (X = S, Se) compounds with Fe substitution for Cd on the tetrahedral sites or for anion deficient $CdCr_2X_4$ (X = S, Se) crystals [20,23,28,29]. The strong anisotropy in the latter case was ascribed to Cr^{2+} ions on the octahedral sites, which appear to compensate the charge of anion vacancies [30,31]. Estimations, however, are not consistent with the presence of a noticeable quantity of Fe^{2+} ions in our $MnCr_2S_4$ single crystals. Indeed, to explain the observed anisotropy in $MnCr_2S_4$ crystals one has to assume the presence of $\sim 4\times10^{-3}$ Fe^{2+} impurity ions. The presence of such an amount of iron impurities in our single crystals seems to be quite unrealistic, because it would exceed that of all possible impurities in the starting materials used for crystal growth by a factor of 20. With respect to the presence of Cr^{2+} ions, which may arise due to sulphur vacancies, it should be noted, that the very low values of the ESR linewidth observed, probably, rule out a considerable amount of anion defects in ‘as grown’ single crystals. Our experiments using heat treatment of the samples in different atmospheres show a strong increase of the resonance linewidth for samples, in which anion vacancies are induced. An analogous effect on the linewidth has been observed in $CdCr_2Se_4$ single crystals due to selenium vacancies [32]. However, the observed influence of sulphur non-stoichiometry on the resonance field for $MnCr_2S_4$ samples from different batches is rather complicated. Therefore we cannot exclude some degree of inversion and presence of a small amount of Mn^{3+} ions on the octahedral sites of the spinel structure, generating magneto-crystalline anisotropy. Another possible reason for the anisotropy may be the partial valence exchange between Mn^{2+} and Cr^{3+} ions producing a small amount of Cr^{2+} and Mn^{3+} ions on their original sites. Verification of the mechanisms which give rise to the strong anisotropy in $MnCr_2S_4$ crystals is in progress and results will be published in a forthcoming paper.

5. Conclusion

We have investigated the ESR properties of single crystals of the ferrimagnet $MnCr_2S_4$. We found a pronounced cubic magneto-crystalline anisotropy with an easy magnetization direction along the ⟨001⟩ axis and a hard magnetization direction along the ⟨111⟩ axis. Large variations of the resonance fields due to the temperature dependence of the magnetocrystalline anisotropy and the magnetization were observed. The anisotropy constants K_1 and K_2 determined from the resonance-field data reach about 10^5 erg/cm^3 at low temperatures. A preliminary analysis of the mechanisms that may contribute to the anisotropy excludes the presence of Fe^{2+} impurity ions and shows a minor role of sulphur vacancies in ‘as grown’ single crystals.

Acknowledgments

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