Hopkinson-Like Effect in Single-Crystalline CdCr₂Se₄ and Cd[Cr₁.₈₉Ti₀.₀₈]Se₄*

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The static (dc) and dynamic (ac) magnetic measurements of CdCr₂Se₄ and Cd[Cr₁.₈₉Ti₀.₀₈]Se₄ showed their ferromagnetic properties with a Curie temperature $T_C \approx 130$ K and revealed on the real component of ac susceptibility curve, the peaks near $T_C$ at 200 Oe, 450 Oe and 1 kOe, characteristic for the Hopkinson ones. The meaningful reduction of saturation moment to 4.73 $\mu_B$/f.u. for Cd[Cr₁.₈₉Ti₀.₀₈]Se₄ suggests the diamagnetic configuration of Ti ions, which dilutes the ferromagnetic sublattice of Cr ones and causes reducing of the energy losses visible on the imaginary components of ac susceptibility curve. Close for zero values of higher susceptibility harmonics above $T_C$ are pointing out to the lack of the spin fluctuations in the paramagnetic state.

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1. Introduction

The magnetization of many compounds shows a peak near the ordering temperature when heating the sample in a fixed (small) magnetic field [1]. This behavior is commonly called the Hopkinson effect [2]. The accepted explanation [3] of this effect is based only on domain wall motion. This mechanism is obviously inapplicable to the case of single-domain particles. However, a thermomagnetic effect which is quite similar to the Hopkinson effect has been experimentally observed in most of the amorphous magnetic materials as well as in some spin glasses where the existence of multi-domain particles is questionable or even practically impossible [2]. In Nd₂Fe₁₄B-type ribbons the existence of a maximum in the thermomagnetic curves of thermally demagnetized samples in low fields was connected with the processes of irreversible rotation of magnetic moments of non-interacting uniaxial single domain particles according to the Stoner–Wohlfarth model [2, 4].

The CdCr₂Se₄ spinel combines the $\alpha$-type semi-conducting and ferromagnetic properties with the Curie temperature $T_C = 142$ K and the Curie–Weiss temperature $\theta_{CW} = 190$ K [5, 6]. Magnetization of CdCr₂Se₄ reaches the full saturation of 5.98 $\mu_B$ per molecule [7]. The ferromagnetic properties of CdCr₂Se₄ are a result of dominating interactions between the nearest-neighbour chromium ions and of weaker superexchange couplings between the more distant chromium ones [8]. The Cr 2p X-ray photoelectron spectra (XPS) of CdCr₂Se₄ showed the spin-orbit splitting between the final Cr 2p₃/2 and Cr 2p₁/2 states of 9.5 eV. The Cr 2p₃/2 states are split into two peaks at 574.2 and 575.2 eV. The peak separation with the binding energy difference $\Delta E$ about 1 eV is typical of the 3d⁵ elements with localized magnetic moment of 3 $\mu_B$ [9]. CdCr₂Se₄ crystallizes in the cubic structure (Fd3m). The X-ray refinements showed that the (Cd) ions have a preference to be located in the tetrahedral sites and the [Cr] ions prefer to be located in the octahedral sites of the spinel structure [10]. In slightly doped with gallium, CdCr₁.₉₈Ga₀.₀₂Se₄ [10], and with vanadium, Cd₀.₉₈Cr₁.₀₂V₀.₀₈Se₄ [11], a step-like structure of the electrical conductivity and a micromagnetic order [12] were observed.

2. Experimental details

The single-crystal X-ray diffraction data were collected on Gemini A Ultra diffractometer equipped with CCD detector and using Mo $K_{\alpha}$ radiation. The structure was refined by the full-matrix least-squares method by means of SHELX-97 program package [13]. Chemical compositions of the single crystals were determined

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non-destructively by energy-dispersive X-ray fluorescence spectrometry (EDXRF) [14]. The samples were excited by an X-ray beam from the air-cooled side-window Rh target of the X-ray tube with Be window of 125 μm thickness and nominal focal spot size of ca. 100 μm (XTF 5011/75, Oxford Instruments, USA). The quantitative EDXRF analysis was performed using the fundamental parameter method based on the Sherman equation [15] and Pella et al. algorithm [16, 17] to calculate the X-ray tube spectrum. The X-ray diffraction revealed a single-phase material with the cubic spinel structure (Fd3m) with a lattice parameter \(a = 1073.3(8)\ \text{pm}\) for CdCr2Se4 and \(a = 1068.32(13)\ \text{pm}\) for Cd[Cr1.89Ti0.08]Se4.

Dc magnetization, ac and dc magnetic susceptibility of the single crystals under study were measured in the zero-field-cooled mode using a Lake Shore 7225 dc magnetometer/ac susceptometer in the temperature range 4.3–300 K and in applied external magnetic fields up to 60 kOe. The in-phase \(\chi_1(T)\) and out-of-phase \(\chi_\prime(T)\) components of the ac fundamental susceptibility were recorded in the temperature range 4.5–160 K using an oscillating field \(H_{ac} = 1\ \text{Oe}\) with frequency of 120 Hz for external magnetic fields \(H_{dc} = 0.100\ \text{Oe}, 200\ \text{Oe}, 450\ \text{Oe}\) and 1 kOe. The signals of the second (\(\chi_2\)) and third (\(\chi_3\)) harmonics were detected at the same temperature range, for the same amplitude and frequency as the ac \(\chi_1\) measurements without an external static magnetic field.

3. Results and discussion

Figures 1–3 show the ferromagnetic order with \(T_C = 130\ \text{K}, \theta_{CW} = 150\ \text{K}\) and the saturation magnetization of 5.91 \(\mu_B/\text{f.u.}\) at 4.5 K and at 60 kOe for CdCr2Se4, and with \(T_C = 129\ \text{K}, \theta_{CW} = 138\ \text{K}\) and the saturation magnetization of 4.73 \(\mu_B/\text{f.u.}\) at 4.3 K and at 60 kOe for Cd[Cr1.89Ti0.08]Se4. The values of \(T_C\) and \(\theta_{CW}\) characterize the long- and short-range superexchange magnetic interactions, respectively. The strongly reduced saturation magnetization for Cd[Cr1.89Ti0.08]Se4 in comparison with the CdCr2Se4 matrix (5.98 \(\mu_B/\text{f.u.}\) [7]) seems to be partially connected with the solution of the magnetic Cr-sublattice by the diamagnetic Ti4+ ions. Other hypothetical possibility is a mixed-spin state of the Cr ions in the \(\text{Cr}_2\) orbital.

The fitting procedure of the Curie–Weiss law [18] shows that the experimental (blue) curve of \(\chi^{-1}(T)\) in Fig. 1 deviates upward from its linear part (red curve). It indicates the diamagnetic temperature independent contribution to the magnetic susceptibility with the value of \(\chi_0 = -1.74 \times 10^{-6}\ \text{cm}^3/\text{g}\) for CdCr2Se4 and of \(\chi_0 = -1.23 \times 10^{-5}\ \text{cm}^3/\text{g}\) for Cd[Cr1.89Ti0.08]Se4, for which the Pearson correlation coefficient \(R\) is over 99% [18]. Usually \(\chi_0\) contains the orbital and Landau diamagnetism, the Pauli and Van Vleck paramagnetism as well as others, as they cannot be separated. Because the CdCr2Se4 matrix is the semiconductor [5] the Landau and Pauli contributions can be neglected.

The ac magnetic susceptibility measurements presented in Figs. 4 and 5 revealed the spectacular peaks for both single crystals under study at 200 Oe, 450 Oe and at 1 kOe on the \(\chi'_1(T)\) curve near \(T_C\), characteristic for the Hopkinson peak. Both \(\chi_\sigma(T)\) (measured at the static magnetic field \(H_{dc} = 1\ \text{kOe}\) and \(\chi'_1(T)\) (measured at the oscillating magnetic field \(H_{ac} = 1\ \text{Oe}\) and at the constant frequency of 120 Hz) show the same ordering temperature \(T_C\), but different magnetic state. With increasing \(H_{dc}\) up to 100 Oe, \(\chi'_1(T)\) correlates well with \(\chi_\sigma(T)\). Starting from 200 Oe, \(H_{dc}\) suppresses the magnetic susceptibility intensity of \(\chi'_1(T)\) showing characteristic peaks at 200 Oe, 450 Oe and at 1 kOe near \(T_C\). This feature could be connected with the processes of irre-
versable rotation of magnetic moments of non-interacting uniaxial single domain particles [2, 4]. Small and positive values of \( \chi''_1(T) \) below \( T_C \) for CdCr\(_2\)Se\(_4\) (Fig. 4) indicate the energy loss, connected, for example, with the magnetic-domain-wall motion or with rotation of magnetization within domains [19]. However, the sample richer in titanium (Fig. 5) is showing the slight energy loss (the values of \( \chi''_1(T) \) are close to zero) which can suggest that in this case the magnetizing processes do not appear.

The second \( \chi_2(T) \) and third \( \chi_3(T) \) harmonics of ac magnetic susceptibility are shown in Fig. 6 for CdCr\(_2\)Se\(_4\) and in Fig. 7 for Cd[Cr\(_{1.89}\)Ti\(_{0.08}\)]Se\(_4\). These higher harmonics have one feature in common: their values are close to zero below \( T_C \) in accordance with the simple molecular field theory [20]. Moreover, zeroing their values above \( T_C \) is the evidence of the lack of the spin fluctuations in the paramagnetic state characteristic, e.g., in case of ZnCr\(_2\)Se\(_4\) [21], ZnCr\(_{2-x}\)Al\(_2\)Se\(_4\) [22] and ZnCr\(_2\)Se\(_4\) diluted with Ga, In and Ce [23].

4. Conclusions

The Hopkinson-like effect using the complex ac dynamic magnetic susceptibility measurements in single-
-crystalline CdCr$_2$Se$_4$ and Cd[Cr$_{1.89}$Ti$_{0.08}$]Se$_4$ ferromagnetic semiconductors was observed. Its existence in a system of non-interacting single-domain particles close to the ordering temperature is probable. One can suggest that the complex ac dynamic magnetic susceptibility is a sensitive tool for the studies of exotic phenomena and fascinating ground states in the materials with the spinel structure.

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References