Title: Hopkinson-like effect in single-crystalline CdCr 2Se 4 and Cd[Cr 1.89Ti 0.08]Se 4

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Hopkinson-Like Effect in Single-Crystalline $CdCr_2Se_4$ and $Cd[Cr_{1.89}Ti_{0.08}]Se_4$*

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The static (dc) and dynamic (ac) magnetic measurements of $CdCr_2Se_4$ and $Cd[Cr_{1.89}Ti_{0.08}]Se_4$ 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 μ_B/f.u. for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$ 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 $Nd_2Fe_{14}B$-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 $CdCr_2Se_4$ spinel combines the p-type semiconducting and ferromagnetic properties with the Curie temperature $T_C = 142$ K and the Curie–Weiss temperature $\theta_{CW} = 190$ K [5, 6]. Magnetization of $CdCr_2Se_4$ reaches the full saturation of 5.98 μ_B per molecule [7]. The ferromagnetic properties of $CdCr_2Se_4$ 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 $CdCr_2Se_4$ showed the spin–orbit splitting between the final Cr $2p_{3/2}$ and Cr $2p_{1/2}$ states of 9.5 eV. The Cr $2p_{3/2}$ states are split into two peaks at 574.2 and 575.2 eV. The peak separation with the binding energy difference ΔE about 1 eV is typical of the $3d^3$ elements with localized magnetic moment of 3 μ_B [9]. $CdCr_2Se_4$ 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, $CdCr_{1.985}Ga_{0.015}Se_4$ [10], and with vanadium, $Cd_{0.87}Cr_{1.93}V_{0.06}Se_4$ [11], a step-like structure of the electrical conductivity and a mictomagnetic 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_α 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 $a = 1073.3(8)$ pm for $CdCr_2Se_4$ and $a = 1068.32(13)$ pm for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$.

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 $\chi_1''(T)$ components of the ac fundamental susceptibility were recorded in the temperature range 4.5–160 K using an oscillating field $H_{ac} = 1$ Oe with frequency of 120 Hz for external magnetic fields $H_{dc} = 0.100$ Oe, 200 Oe, 450 Oe and 1 kOe. The signals of the second (χ_2) and third (χ_3) harmonics were detected at the same temperature range, for the same amplitude and frequency as the ac χ_1 measurements without an external static magnetic field.

3. Results and discussion

Figures 1–3 show the ferromagnetic order with $T_C = 130$ K, $\theta_{CW} = 150$ K and the saturation magnetization of 5.91 μ_B/f.u. at 4.5 K and at 60 kOe for $CdCr_2Se_4$, and with $T_C = 129$ K, $\theta_{CW} = 138$ K and the saturation magnetization of 4.73 μ_B/f.u. at 4.3 K and at 60 kOe for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$. The values of T_C and θ_{CW} characterize the long- and short-range superexchange magnetic interactions, respectively. The strongly reduced saturation magnetization for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$ in comparison with the $CdCr_2Se_4$ matrix (5.98 μ_B/f.u. [7]) seems to be partially connected with the solution of the magnetic Cr-sublattice by the diamagnetic Ti^{4+} ions. Other hypothetical possibility is a mixed-spin state of the Cr ions in the t_{2g} orbital.

The fitting procedure of the Curie–Weiss law [18] shows that the experimental (blue) curve of $\chi_\sigma^{-1}(T)$ 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 $\chi_0 = -1.74 \times 10^{-6}$ cm^3/g for $CdCr_2Se_4$ and of $\chi_0 = -1.23 \times 10^{-5}$ cm^3/g for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$, for which the Pearson correlation coefficient R is over 99% [18]. Usually χ_0 contains the orbital and Landau diamagnetism, the Pauli and Van Vleck paramagnetism as well as others, as they cannot be separated. Because the $CdCr_2Se_4$ 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

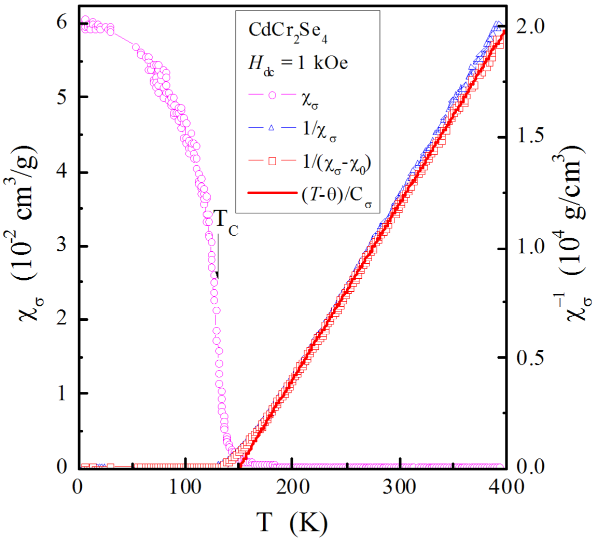

Fig. 1. Dc magnetic susceptibility χ_σ and inverse susceptibility $1/\chi_\sigma$ vs. temperature T at 1 kOe for $CdCr_2Se_4$. T_C is marked by arrow.

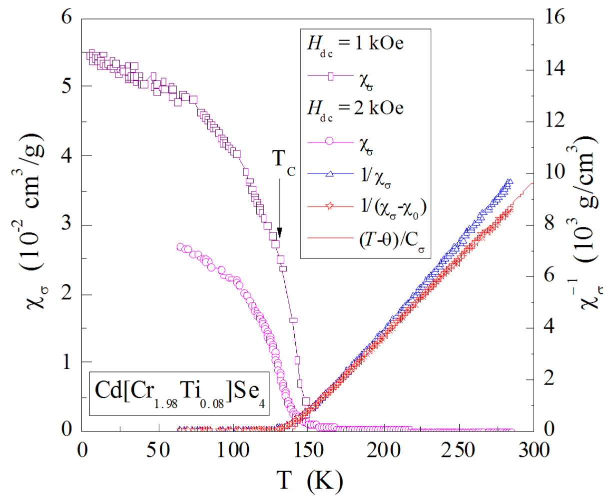

Fig. 2. Dc magnetic susceptibility χ_σ and inverse susceptibility $1/\chi_\sigma$ vs. temperature T at 1 kOe and 2 kOe for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$. T_C is marked by arrow.

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 $H_{dc} = 1$ kOe) and $\chi_1'(T)$(measured at the oscillating magnetic field $H_{ac} = 1$ 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-

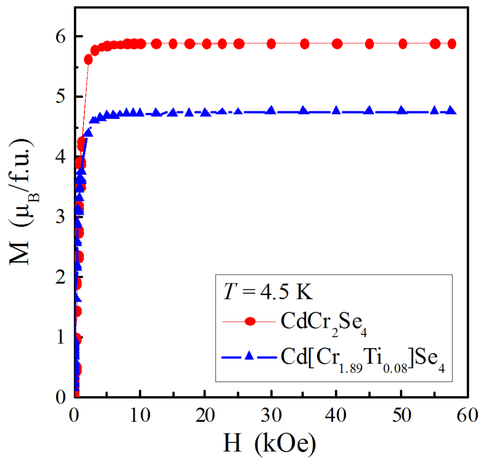

Fig. 3. Magnetization M vs. magnetic field H at 4.5 K.

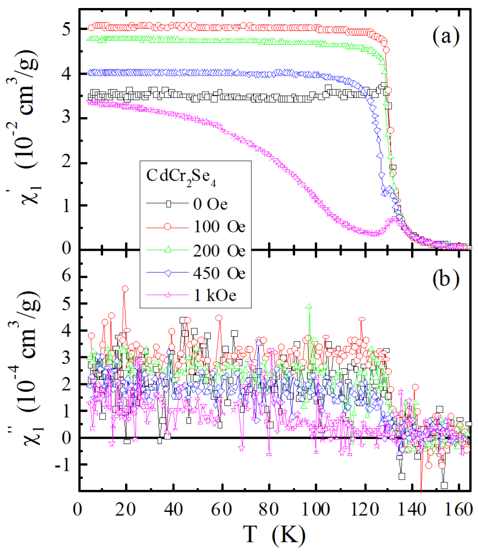

Fig. 4. In phase χ_1' (a) and out of phase χ_1'' (b) components of ac magnetic susceptibility vs. temperature T for $CdCr_2Se_4$ recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz for external magnetic fields H_{dc} changing from 0 to 1 kOe.

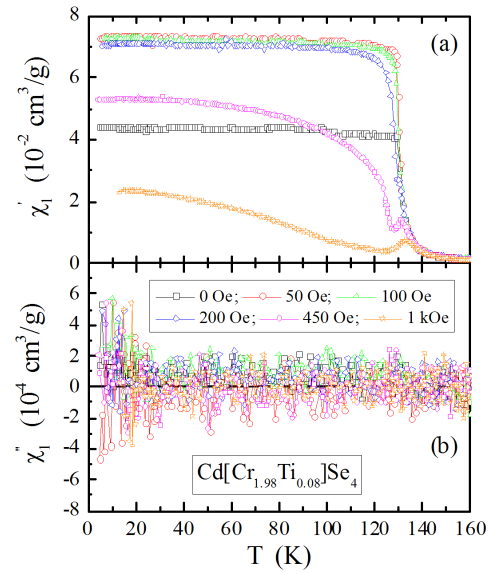

Fig. 5. In phase χ_1' (a) and out of phase χ_1'' (b) components of ac magnetic susceptibility vs. temperature T for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$ recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz for external magnetic fields H_{dc} changing from 0 to 1 kOe.

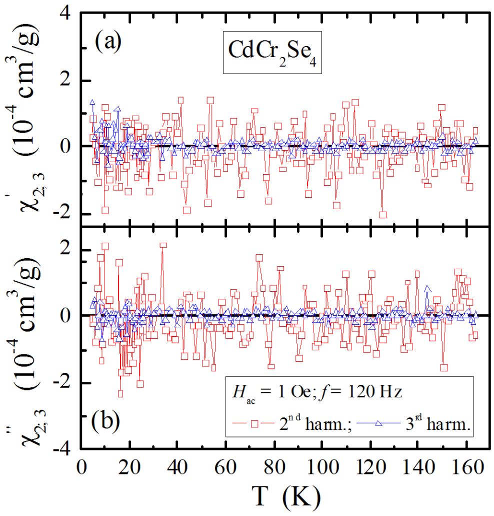

Fig. 6. In phase $\chi_{2,3}'$ (a) and out of phase $\chi_{2,3}''$ (b) components of second and third harmonics of zero field susceptibility vs. temperature T for $CdCr_2Se_4$ recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz.

versible 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 $CdCr_2Se_4$ (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 $CdCr_2Se_4$ 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 $ZnCr_2Se_4$ [21], $ZnCr_{2-x}Al_xSe_4$ [22] and $ZnCr_2Se_4$ diluted with Ga, In and Ce [23].

4. Conclusions

The Hopkinson-like effect using the complex ac dynamic magnetic susceptibility measurements in single-

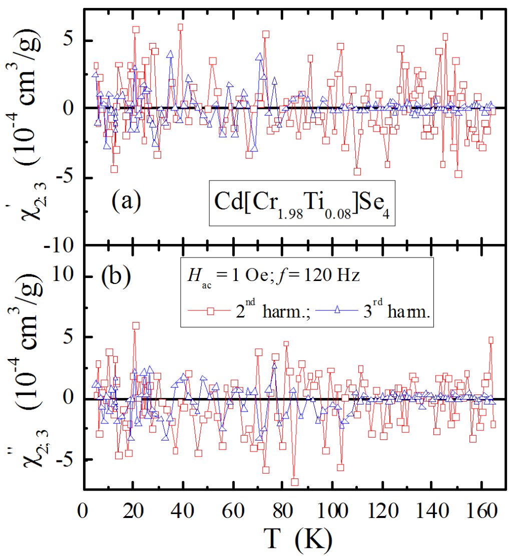

Fig. 7. In phase $\chi'_{2,3}$ (a) and out of phase $\chi''_{2,3}$ (b) components of second and third harmonics of zero field susceptibility vs. temperature T for $Cd[Cr_{1.89}Ti_{0.08}]Se_4$ recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz.

-crystalline $CdCr_2Se_4$ 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.

Acknowledgments

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