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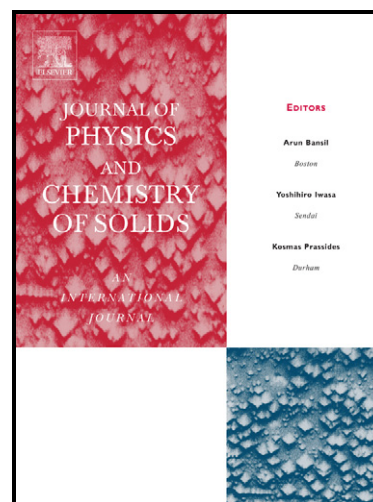
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# Specific heat and magnetic susceptibility of single-crystalline $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$ ( $x = 0.15, 0.23$ )

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## ABSTRACT

A correlation between the second critical field  $H_{c2}$  of the helix to paramagnetic transition and the magnetic specific heat  $C$ -peak was found in  $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$  spinel single crystals with  $x = 0.15, 0.23$ . The specific heat peak is anomalously sharp for all finite magnetic fields used here and this points to a first order magneto-structural transition (from cubic to tetragonal symmetry). The  $C(T)$ -peak is increasingly suppressed as the external field increases. Approaching the Neel temperature  $T_N$ , a broad ac-magnetic susceptibility peak is observed for zero dc-magnetic field. That peak does not show an energy loss and thus points towards a return to a second order type of transition. The magnetic contribution to the specific heat displays a sharp peak at  $T_N$  and is maximal at the spin fluctuation temperature  $T_{sf} = 34$  K.  $T_{sf}$  is related to the maximum of the magnetic susceptibility at  $T_m = 40$  K (at 50 kOe) in the spin fluctuation region, as evidenced by the entropy exceeding 90% of the entropy calculated classically for the complete alignment of the Cr spins,  $(2-x)R\ln(2S+1)$ . The X-ray photoelectron spectroscopy (XPS) data indicate that Al-substitution does not affect  $\text{Cr}^{3+} 3d^3$  electronic configuration.

**Keywords:** A. chalcogenides; B. crystal growth; C. photoelectron spectroscopy; D. magnetic properties; D. specific heat

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## 1. Introduction

It is well known in literature that  $\text{ZnCr}_2\text{Se}_4$  spinel is a matrix of various diluted systems where effects of site disorder, lattice frustration and random distribution of spin interactions create novel potential applications in spin-based electronic technology.  $\text{ZnCr}_2\text{Se}_4$  reveals a spectacular transition to an antiferromagnetic (AFM) state at Néel temperature  $T_N = 20$  K with the dominating ferromagnetic (FM) interactions evidenced by large positive Curie-Weiss temperature  $\theta_{CW} = 115$  K [1,2] and accompanied by a structural transformation from cubic  $Fd\bar{3}m$  to tetragonal  $I4_1/amd$  symmetry with a small contraction along the  $c$  axis [3], although, the structural investigations using synchrotron radiation defined the latter symmetry as orthorhombic  $Fddd$  [4]. Previous neutron-diffraction investigations [1,2] of  $\text{ZnCr}_2\text{Se}_4$  spinel showed a helical AFM spin structure below ordering temperature having an FM arrangement in the (001) planes with a turning angle of  $42^\circ$  between the spins in adjacent (001) planes. Recently, sharp first-order phase transition anomalies in specific heat and negative thermal expansion (NTE) strongly suppressed by external magnetic fields at  $T_N$  were found [5]. Moreover, a metamagnetic transition at critical field  $H_{c1}$  of about 10 kOe for  $T = 2$  K, a breakdown of the conical spin arrangement at the critical field  $H_{c2}$  of about 65 kOe for  $T = 2$  K, and full saturation magnetisation of about  $3\mu_B$  per Cr ion above  $H_{c2}$  for the FM state in  $\text{ZnCr}_2\text{Se}_4$  single crystal occurred [5]. At a temperature smaller than  $T_N$ , the zero-field-cooling

(ZFC) and field-cooling (FC) susceptibilities diverge, which suggests a spin frustration effect [5]. The complex ac dynamic magnetic susceptibility used to study the influence of temperature on critical fields in polycrystalline  $\text{ZnCr}_2\text{Se}_4$  spinel [6] showed a parallel spin coupling in FM clusters in the range between  $T_N = 20.7$  K and  $\theta_{CW} = 55.1$  K as well as a strong drop of the value of the second critical field  $H_{c2}$  with temperature suggesting a spin frustration of the re-entrant type.

Magnetic investigations carried out on the stoichiometric single crystals of the  $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$  spinel system with  $x = 0.15$  and  $0.23$  [7] and non-stoichiometric polycrystalline  $\text{Zn}_x\text{Cr}_y\text{Al}_z\text{Se}_4$  spinels ( $0.13 \leq z \leq 0.55$ ) [8,9] showed similar values of  $T_N$ ,  $\theta_{CW}$  and effective magnetic moments (Fig. 1). They also revealed saturation magnetic moment appeared to be decreased with rising Al- content (Fig. 1). For large Al-substitution, i.e. for  $z = 0.55$ , a spin-glass-like behaviour of cluster type with randomly oriented magnetic moments was observed as the ZFC-FC splitting went up to freezing temperature  $T_f = 11.5$  K and the critical fields connected both with a transformation of the AFM spin spiral via conical magnetic structure into FM phase disappeared [8].

The present contribution reports XPS, magnetic and specific heat measurements for  $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$  compensated spin array harbouring mixed couplings doped with the octahedrally coordinated nonmagnetic Al ions with  $x = 0.15$  and  $0.23$ . The novelty in this work are the specific heat studies, which are related both to the critical fields and critical temperature of the magnetic phase transitions. Therefore, an anomalous sharpness of the magnetic and specific heat peaks at higher magnetic fields as well as the correlation between the spin fluctuation temperature and the temperature corresponding to the maximum of magnetic susceptibility in the paramagnetic (PM) state were the main reason to revisit the  $\text{ZnCr}_{0.85}\text{Al}_{0.15}\text{Se}_4$  and  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$  single crystals.

## 2. Experimental

### 2.1. Synthesis and crystal structure

Single crystals of  $\text{ZnCr}_2\text{Se}_4$  spinel admixed with Al ions were grown from binary selenides  $\text{ZnSe}$  and  $\text{Al}_2\text{Se}_3$  by the chemical vapour transport method with anhydrous  $\text{CrCl}_3$  as the transporting agent. The method has been described in detail elsewhere [7]. Presence of aluminium in the obtained single crystals was checked by wavelength-dispersive X-ray fluorescence spectrometry (PW1410, Philips, Almelo, The Netherlands) with the following measurement conditions: side-window silver target X-ray tube operated at 50kV and 40mA; vacuum;  $K_\alpha$  lines; flow-proportional counter (counter gas 90 % Ar + 10 %  $\text{CH}_4$ ) for Al and Cr, flow-proportional counter with scintillation counter for Zn and Se; LiF(200) analyzing crystal for Zn, Cr and Se, PET(002) for Al; 40s counting time for Zn, Cr, Se and 100s for Al. Crystal structure determinations were performed with graphite monochromated Mo  $K_\alpha$  radiation using a KM-4 Xcalibur single-crystal diffractometer (Oxford Diffraction). The structure refinement was performed using the SHELXL-97 program package [10]. The compositions studied in this article are the same as reported in [7].

### 2.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra were taken using a PHI 5700/660 Physical Electronic spectrometer with monochromated Al  $K_\alpha$  radiation. The photoelectron spectra were analyzed by a hemispherical mirror analyzer with energy resolution of about 0.3 eV. In order to obtain free of contamination fresh surface, the samples were scraped in situ in  $10^{-10}$  hPa vacuum. Overviews of the binding energy in the range -2 to 1400 eV and the core-level characteristic peaks for Cr 2p have been measured. The background was subtracted using the Tougaard's approximation.

### 2.3. Magnetic and specific heat measurements

The ac mass susceptibility was measured using a Lake Shore 7225 ac susceptometer up to almost 60 kOe in the temperature range 4.2÷300 K. Specific heat was measured with Quantum Design Physical Properties Measurement System (QD-PPMS) heat capacity option in temperature range 1.8÷300 K and at magnetic field up to 70 kOe.

## 3. Results and discussion

### 3.1. X-ray photoelectron spectroscopy (XPS)

Figure 2 shows the Cr 2p XPS spectra of  $\text{ZnCr}_2\text{Se}_4$  and  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$  single crystals with 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  $\Delta E$  about 1 eV is typical of the 3d elements with localized magnetic moment of  $3 \mu_B$ . Such a value of  $\Delta E$  was reported for  $\text{ZnCr}_2\text{Se}_4$  and for a number of other chalcogenide spinels [11,12]. It is important to notice that the splitting of the  $2p_{3/2}$  states can be observed experimentally only for the 3d elements with localized magnetic moments larger than  $2 \mu_B$  [13,14]. Moreover, a linear relationship has been reported between the magnitude of the splitting of the  $2p_{3/2}$  levels and the valence state of the 3d transition metals [13]. Based on these findings, it can be concluded that Cr ions in the  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$  single crystal have the electronic state  $\text{Cr}^{3+} 3d^3$ , independently of the Al-substitution.

### 3.2. Magnetic properties

The results of temperature dependences of real  $\chi'$  and imaginary  $\chi''$  components of ac magnetic susceptibility and specific heat at different external magnetic fields as well as the ac magnetic susceptibility versus magnetic field at different temperatures are presented in Figs. 3-5 for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$  and in Figs. 6-8 for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ . For  $H_{dc} = 0$ ,  $\chi'(T)$  manifests in

Fig. 3 a broad peak on approaching the Néel temperature  $T_N$  accompanied with lack of loss of energy visible in  $\chi''(T)$ , and points towards a second-order transition typical for conventional antiferromagnets. Similar behaviour has been observed for  $\text{ZnCr}_2\text{Se}_4$  [5,6] and  $\text{Zn}_x\text{Cr}_y\text{Al}_z\text{Se}_4$  [7-9] spinels. On the other hand, the peak in  $C(T)$  for  $H_{dc} = 0$  in Fig. 4 at  $T_N$  is anomalously sharp and points towards a first-order transition in accordance with the structural transformation from cubic  $Fd\bar{3}m$  to tetragonal  $I4_1/amd$  symmetry [3]. Application of magnetic field anomalously narrows the peak in  $\chi'(T)$  curve in Fig. 3, especially, for  $H_{dc} \geq 30$  kOe, and its intensity decreases at lower temperatures as in the case of specific heat peaks suggesting the first-order transition accompanied with a rapid energy lost visible in  $\chi''(T)$ . At 50 kOe, an additional broad peak at  $T_m$  in  $\chi'(T)$  occurs, revealing the FM order in the PM state. The PM region is characterized by large positive Curie-Weiss (CW) temperature of 114 K (see Table 1). In the case of specific heat, the increasing magnetic field consistently suppresses the peak in  $C(T)$  curve in Fig. 4 and shifts it to lower temperatures pointing towards the first-order transition.

Figure 5 shows the ac magnetic susceptibility versus magnetic field at different temperatures for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$  with the critical fields indicated by  $H_{c1}$  and  $H_{c2}$ . The first critical field,  $H_{c1}$ , connected with the metamagnetic transition and the breakdown of the spiral spin structure [3,5], slightly decreases with temperature while the second critical field,  $H_{c2}$ , connected with the breakdown of the conical spin arrangement [5,6], drops strongly with temperature. Beyond  $H_{c2}$ , magnetization reaches the FM state [7-9], and above  $T_N$ , both critical fields disappear. Low sensitivity to temperature of  $H_{c1}$  correlates well with the AFM order in the orthorhombic structure. On the other hand, strong sensitivity of  $H_{c2}$  to temperature means that FM coupling is weaker than AFM one, although the FM short-range interactions exist far above  $T_N$  in the cubic (spinel) structure reaching a maximum at  $T_m$ . It means that the increasing external magnetic fields extends the FM order from one side and



shifts both the AFM order and structural transformation from the other towards the lower temperatures.

The results for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ , presented in Figs. 6-8, are similar to the ones for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$ , and they are considered in the context of increasing Al content in the sample. The values of  $T_N$  at 10, 30 and 50 kOe (Figs. 3 and 6), a peak of  $C(T)$  at 20, 40 and 60 kOe (Figs. 4 and 7) and  $H_{c1} = 12.5$  kOe at 4.3, 6 and 12 K are the same for both single crystals (Figs. 5 and 8). Only  $H_{c2}$  at 4.3 K has a larger value for a sample with  $x = 0.15$  compared to  $x = 0.23$ . It means that the larger Al-content, the lower value of  $H_{c2}$  at low temperatures. Similar results were found for  $\text{Zn}_x\text{Sb}_y\text{Cr}_z\text{Se}_4$  [15]. Next, for  $\text{Zn}_x\text{Sn}_y\text{Cr}_z\text{Se}_4$  the values of  $H_{c1}$  were of the same order, while the values of  $H_{c2}$  rapidly decreased with Sn-substitution, especially, when Sn-ions occupied octahedral sites in the spinel structure [16]. It is worth noticing that the peak in  $C(T)$  in Fig. 7 is fully suppressed by a magnetic field of 70 kOe where the helical spin arrangement is completely destroyed, indicating that the FM order dominates in the whole temperature range. Similar behaviour of the specific heat peaks and magnetic transitions may suggest that the strong magnetic field retains the cubic spinel structure in the whole range of temperatures, removing the structural instability observed in weak magnetic fields. This idea, of course, requires X-ray examinations in the strong magnetic field.

### 3.3. Specific heat studies

Figure 9 displays specific heat in zero magnetic field versus temperature in wide  $T$ -range for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ . Above 50 K,  $C(T)$  can be well fitted by expression [17]:

$$C(T) = 9Rn \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where  $R$  is the universal constant,  $n = 7$  is the number of atoms in the formula unit and  $\theta_D$  is Debye temperature. The least-square fit of this expression to the experimental data yield

reasonable values of Debye temperature  $\theta_D$ :  $\sim 358$  K and  $315$  K for  $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$  crystals with  $x = 0.15$  and  $0.23$ , respectively. The data of  $C(T)$  for  $B = 0$  obtained for the sample with  $x = 0.15$  are very similar to those obtained for the sample with  $x = 0.23$ , so they are not presented here. The  $\theta_D$  values are of the same order for both compounds, although they are slightly higher for the one richer in chromium. We attribute the differences of  $\theta_D$  to different elastic properties (bulk modules) of both spinels. On the other hand, the coupling between the spins and lattice may be realized via an exchange-striction mechanism similar to a spin-Peierls transition [5]. This results from the fact that volume energy ( $-pV$ ) correlates to Zeeman energy ( $-\sigma H$ ), because the Al-doped unit cell has a slight distortion visible in the anion parameter  $u$ , and its volume ( $V$ ) is larger in comparison with the  $\text{ZnCr}_2\text{Se}_4$  matrix (see Table 1). In this case, Al-doping should act as negative crystal pressure ( $-p$ ) since the ionic radius of  $\text{Al}^{3+}$  is smaller than the  $\text{Cr}^{3+}$  one [18].

In the temperature region of  $T < \sim 50$  K, the deviation observed between the measured and calculated  $C(T)$  data can be attributed to the magnetic ordering state in both compounds at  $T < T_N$  and high energy spin fluctuations. The evidence for the magnetic phase transition (strongly field dependent) results from either the magnetic or specific heat data (c.f. Figs. 6 and 7), whereas the  $\chi'(T)$  component of ac magnetic susceptibility clearly shows a broad maximum at  $T_m \sim 40$  K and at  $50$  kOe for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$  (see Table 1), which supports the high energy spin fluctuations. The inset to Fig. 9 shows the magnetic contribution  $\Delta C$  to specific heat, where the difference  $\Delta C = C_{\text{exp}} - C$  expresses the measured specific heat reduced by the calculated one on the base of the Debye theoretical model (Eq. 1).  $\Delta C$  displays a sharp peak at  $T = T_N$  and a maximum at  $\sim 34$  K, characteristic for magnetic fluctuations. For  $T < T_N$ ,  $\Delta C(T)$  can be described by the expression for an anisotropic spiral structure with an activation gap in magnon dispersion [19]  $\Delta C \sim T^3 \exp(-E_g/k_B T)$  and the spin fluctuation contribution to  $\Delta C$  of  $\delta T^3 \ln(T/T_{\text{sf}})$ , with the spin fluctuation temperature  $T_{\text{sf}} = \sim 34$  K.

Figure 10 shows entropy  $S(T) = \int_0^T \frac{C(T)}{T} dT$  calculated at different magnetic fields  $B$  for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$  (the entropy  $S(T)$  is the same for the sample with  $x = 0.23$ , and it is not presented in this paper).  $S(T)$  goes up slowly to zero as  $T \rightarrow 0$  in order to meet the third thermodynamic law. At temperature  $T_N = 21.3$  K ( $B = 0$ ), the value of the magnetic and phonon contribution to the entropy is only  $\sim 8.2$  J/(mol·K), i.e., much lower than the magnetic contribution  $S_m = (2-x)R\ln(2S+1) = 21.31$  J/(mol·K) calculated per molecule for  $S = 3/2$  of  $\text{Cr}^{3+}$ . The values of  $S_m$  for the spinels under study and the  $\text{ZnCr}_2\text{Se}_4$  matrix (for comparison) are collected in Table 1. Figures 4 and 7 clearly show that application of magnetic fields strongly suppresses the magnetic transition in doped  $\text{ZnCr}_2\text{Se}_4$  (the same effect has been observed for pure  $\text{ZnCr}_2\text{Se}_4$  [5]) and shifts the peak in  $C/T$  to lower temperatures. The anomaly is fully suppressed by the field of 7 T. To estimate the magnetic contribution to entropy  $S$ , we calculated magnetic entropy  $\Delta S$  at  $T_N$ , by integrating  $[C(T, B = 0) - C(T, B = 7 \text{ T})]/T$  over the transition region, which is only  $\sim 6$  % of the full magnetic entropy expected for the complete alignment of the Cr spins. Almost the same result has been obtained recently for  $\text{ZnCr}_2\text{Se}_4$  [5]. This anomaly was interpreted in Ref. 5 as a result of spin fluctuations in the paramagnetic regime. Our specific heat data fully confirm this explanation. We also note that the alloying does not significantly change magnetic properties of the  $\text{ZnCr}_2\text{Se}_4$  sample.

Figures 11 and 12 show the standard procedure with metamagnetic transitions to plot the phase diagrams  $H_c$  vs.  $T$ ,  $T_N$  vs.  $H$  and  $C_m$  vs.  $H$  for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$  and  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ . Metamagnetic threshold connected with the first critical field  $H_{c1}$  does not depend on temperature below  $T_N$  and it does not correlate with specific heat for both single crystals. On the other hand, both diagrams show a strict correlation between the second critical field  $H_{c2}$ , Néel temperature  $T_N$  and the temperature position of specific heat peak  $C_m$  suggesting that the

structural instability can be removed by a magnetic field, because a magnetostrictive coupling is possible in this case.

#### 4. Conclusions

The XPS spectra of the  $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$  single crystals with  $x = 0.15$  and  $0.23$  revealed the binding energy difference of about 1 eV characteristic for 3d elements with localized magnetic moment of  $3 \mu_B$ . This finding is fully consistent with the results of bulk magnetic measurements. The first critical field connected with the metamagnetic transition and the breakdown of the spiral spin structure is temperature-independent below  $T_N$  and it does not correlate with specific heat for both single crystals under study. The second critical field connected with the breakdown of the conical spin arrangement strongly depends on temperature and the magnetic field applied. It correlates well with the magnetic and specific heat transitions. The values of the Debye temperature  $\theta_D$ , estimated from the Debye theory, are of the same order for both compounds, although they are slightly higher for the one richer in chromium. These differences in  $\theta_D$  may suggest their different elastic properties allowing the magnetostrictive coupling between magnetic and lattice excitations. Estimation of the magnetic contribution to specific heat showed a maximum at 34 K, characteristic for magnetic fluctuations, also visible in the ac magnetic susceptibility with the broad maximum at 40 K and in static magnetic field of 50 kOe. The magnetic and specific heat investigations of the single crystals under study provide experimental evidence that the structural transformation is inextricably linked to the magnetic order.

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## Figure captions

**Fig. 1.** The dependence of the Néel ( $T_N$ ), freezing ( $T_f$ ) and saturation magnetization ( $\mu_{\text{sat}}$ ) on Al content in single-crystalline  $\text{ZnCr}_{2-x}\text{Al}_x\text{Se}_4$  [7] and polycrystalline  $\text{Zn}_x\text{Cr}_y\text{Al}_z\text{Se}_4$  [8] spinels.

**Fig. 2.** Cr 2p – XPS spectra of the  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$  and  $\text{ZnCr}_2\text{Se}_4$  single crystals.

**Fig. 3.** Real  $\chi'$  and imaginary  $\chi''$  components of ac magnetic susceptibility vs. temperature  $T$  recorded at  $H_{\text{ac}} = 1$  Oe with  $f = 120$  Hz taken at different external magnetic fields for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$ . The Néel  $T_N$  and  $T_m$  temperatures are indicated by arrows.

**Fig. 4.** Specific heat,  $C$ , versus temperature  $T$  taken at different external magnetic fields for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$ .

**Fig. 5.** Ac magnetic susceptibility,  $\chi_{\text{ac}}$ , vs. static magnetic field  $H$  recorded at internal oscillating magnetic field  $H_{\text{ac}} = 1$  Oe with internal frequency  $f = 120$  Hz taken at different temperatures for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$ . The critical fields  $H_{c1}$  and  $H_{c2}$  are indicated by arrows.

**Fig. 6.** Real  $\chi'$  and imaginary  $\chi''$  components of ac magnetic susceptibility vs. temperature  $T$  recorded at  $H_{\text{ac}} = 1$  Oe with  $f = 120$  Hz taken at different external magnetic fields for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ . The Néel  $T_N$  and  $T_m$  temperatures are indicated by arrows.

**Fig. 7.** Specific heat,  $C$ , versus temperature  $T$  taken at different external magnetic fields for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ .

**Fig. 8.** Ac magnetic susceptibility,  $\chi_{ac}$ , vs. static magnetic field  $H$  recorded at internal oscillating magnetic field  $H_{ac} = 1$  Oe with internal frequency  $f = 120$  Hz taken at different temperatures for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ . The critical fields  $H_{c1}$  and  $H_{c2}$  are indicated by arrows.

**Fig. 9.** Specific heat  $C$  vs. temperature  $T$  in zero magnetic field for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$  and the

best fit of Debye expression (solid red line),  $C(T) = 9Rn \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$ , to the experimental data denoted as  $C_{exp}$  (circles). Inset: magnetic contribution  $\Delta C = C_{exp} - C$  to the specific heat vs. temperature  $T$ . In the temperature region  $T < T_N$ ,  $\Delta C(T)$  expresses magnetic contribution  $\Delta C \sim T^3 \exp(-E_g/k_B T)$  due to anisotropic spiral structure with an activation gap in magnon dispersion (dashed red line) and the spin fluctuation contribution  $\Delta C \sim \delta T^3 \ln(T/T_{sf})$ , with the spin fluctuation temperature  $T_{sf} = \sim 34$  K (denoted by arrow).

**Fig. 10.** Entropy  $S$  vs. temperature  $T$  at different magnetic fields  $B$  for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$ .

**Fig. 11.** The phase diagrams for  $\text{ZnCr}_{1.85}\text{Al}_{0.15}\text{Se}_4$ : critical fields  $H_{c1}$  and  $H_{c2}$  vs. temperature  $T$ , Néel temperature  $T_N$  vs. magnetic field  $H$  and temperature position of specific heat peak  $C_m$  vs. magnetic field  $H$ .

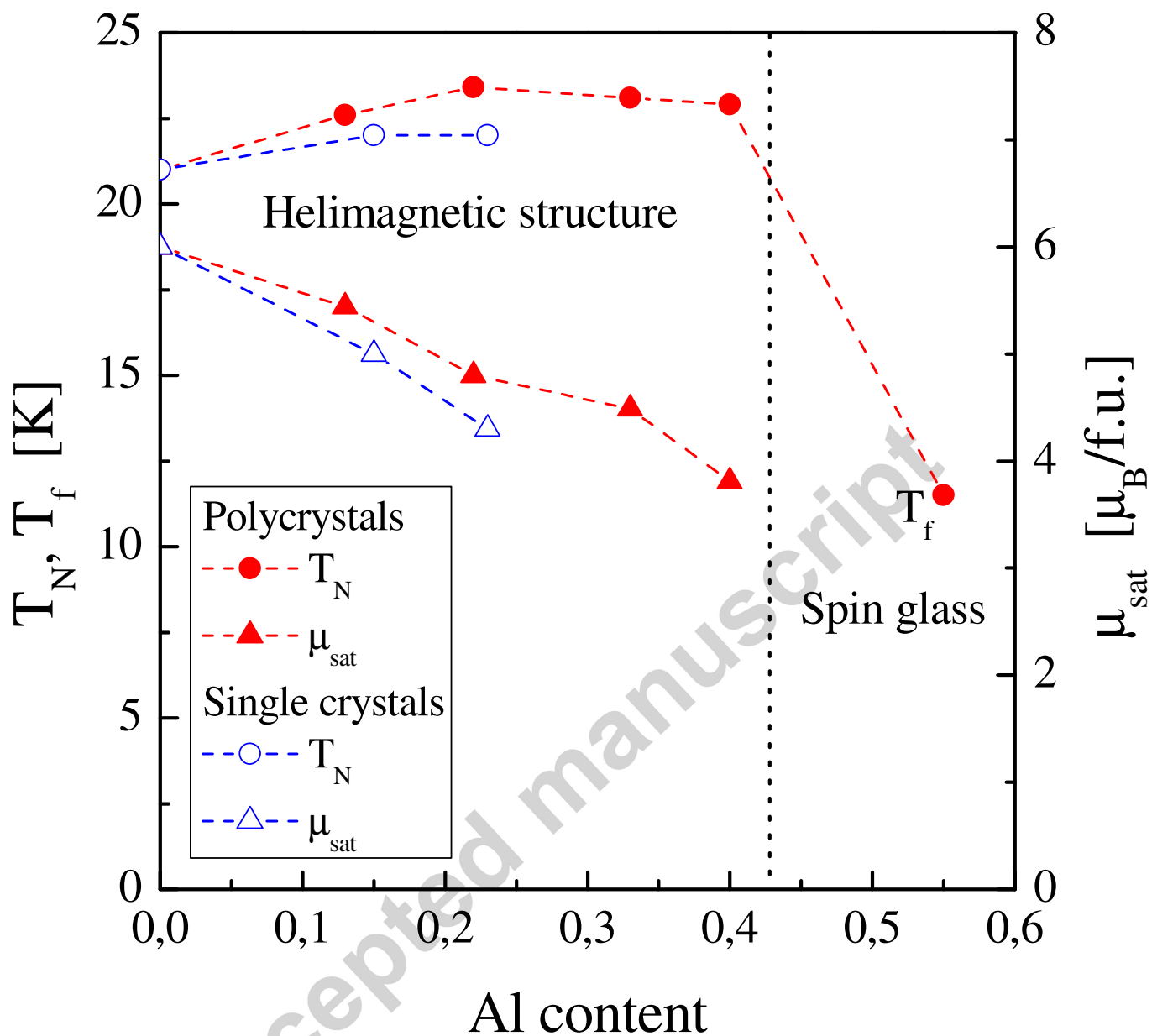
**Fig. 12.** The phase diagrams for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ : critical fields  $H_{c1}$  and  $H_{c2}$  vs. temperature  $T$ , Néel temperature  $T_N$  vs. magnetic field  $H$  and temperature position of specific heat peak  $C_m$  vs. magnetic field  $H$ .

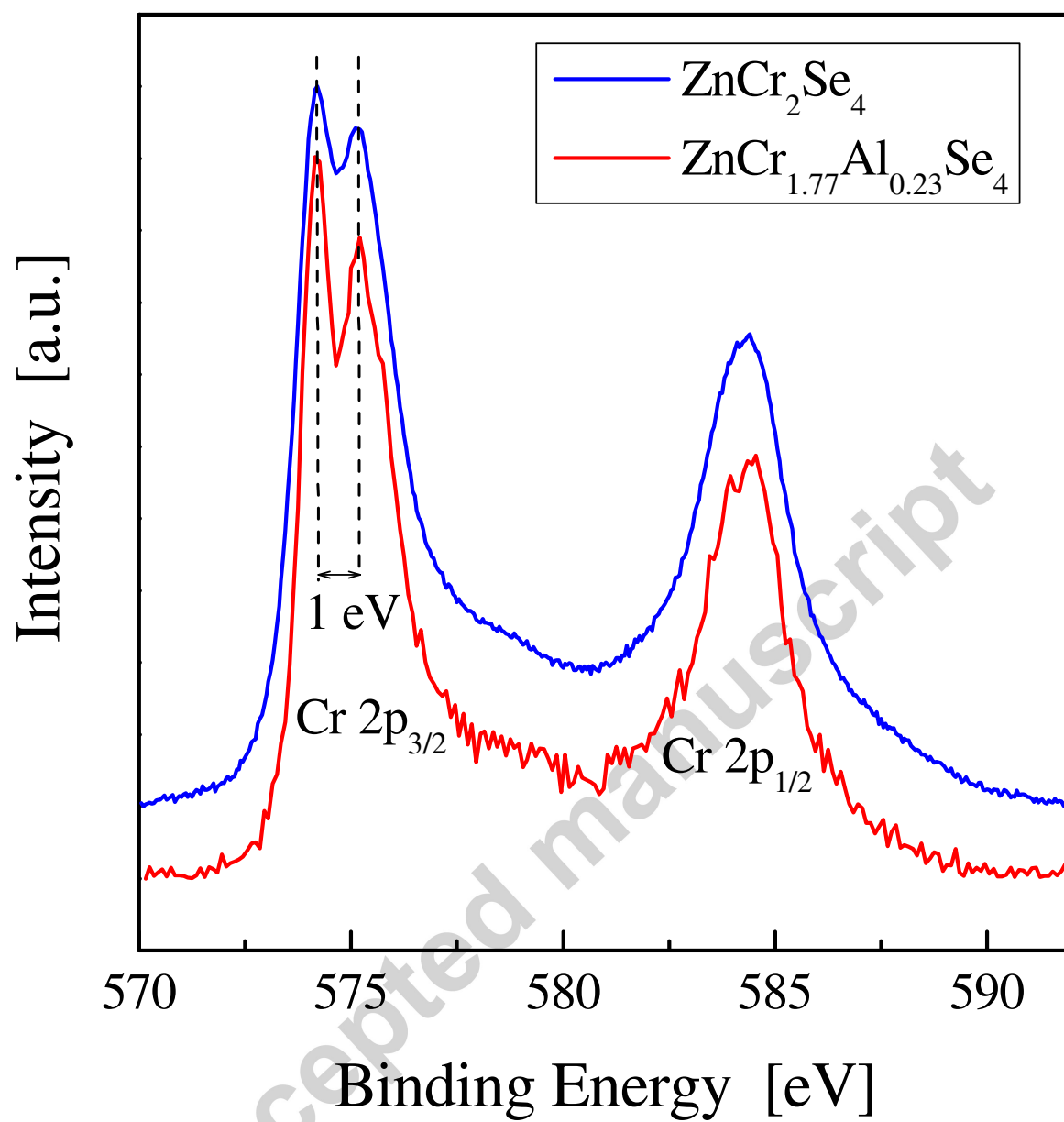


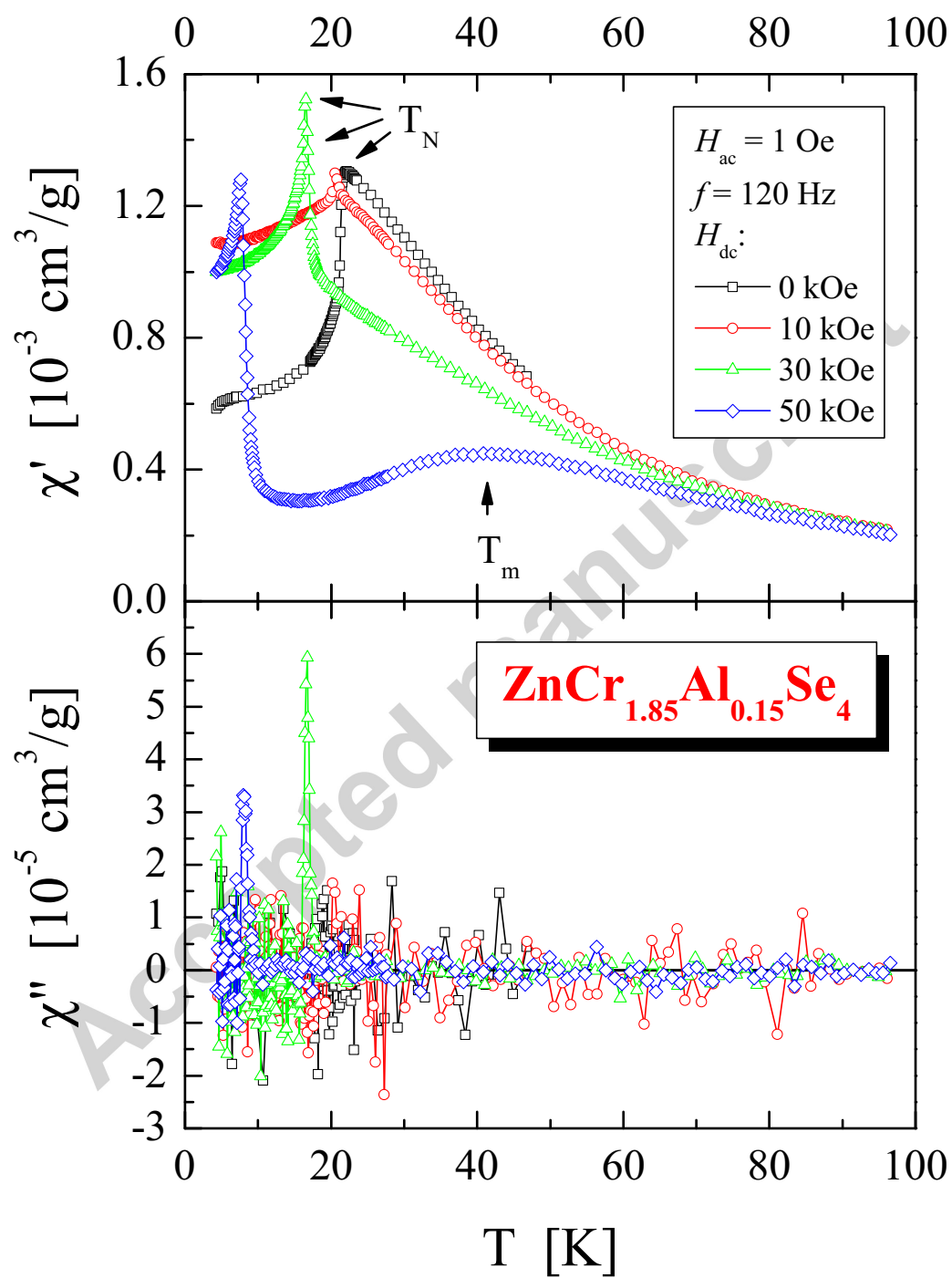
**Highlights**

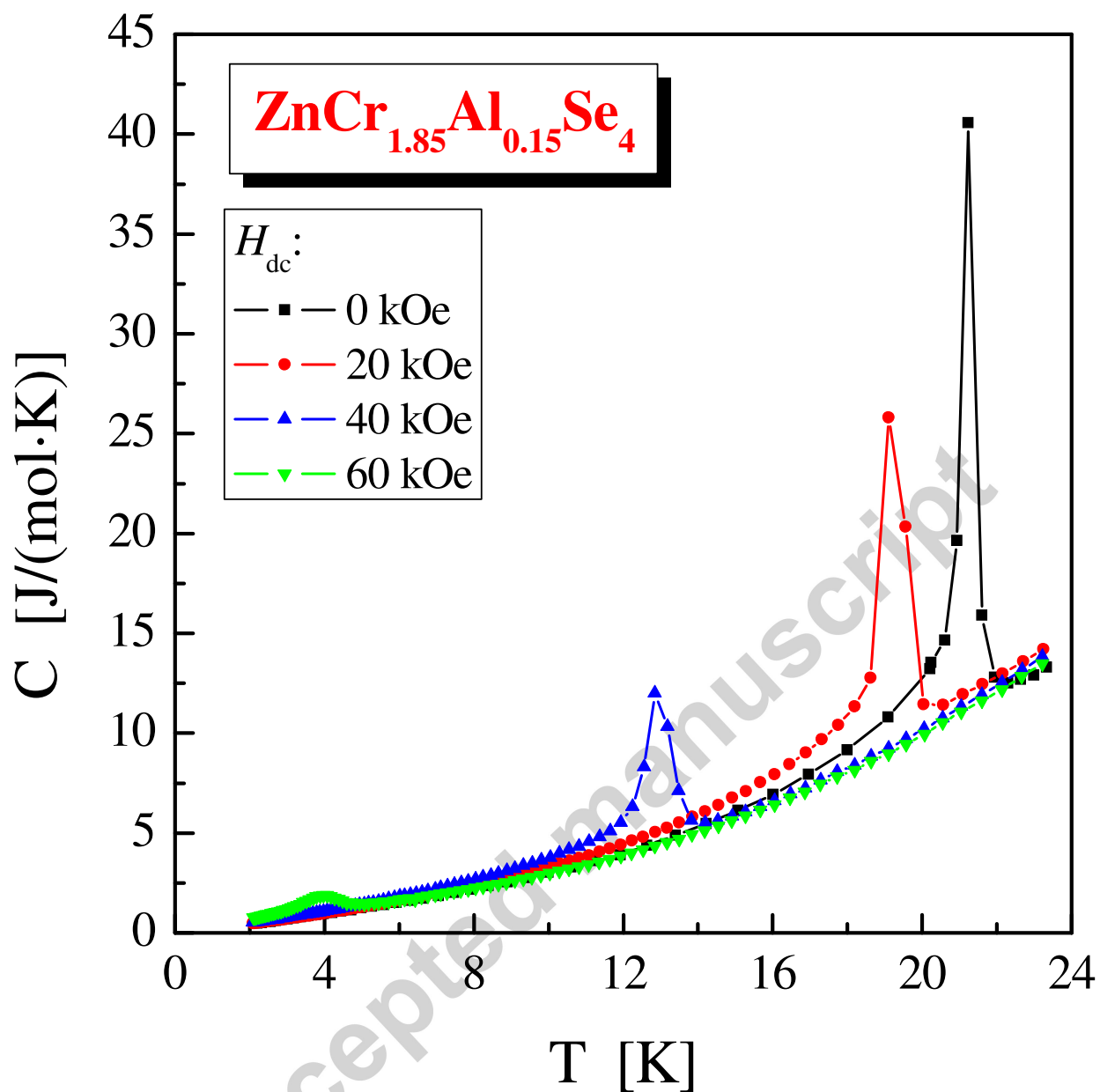
> Al-substitution does not affect the  $\text{Cr}^{3+} 3d^3$  electronic configuration. >  $\chi''(T)$  reveals energy loss only in the case of the first-order transition. > The larger Al-content, the lower value of  $H_{c2}$  at low temperatures. > Larger Al-content makes easier the transfer of phonon momentum to the electron gas.

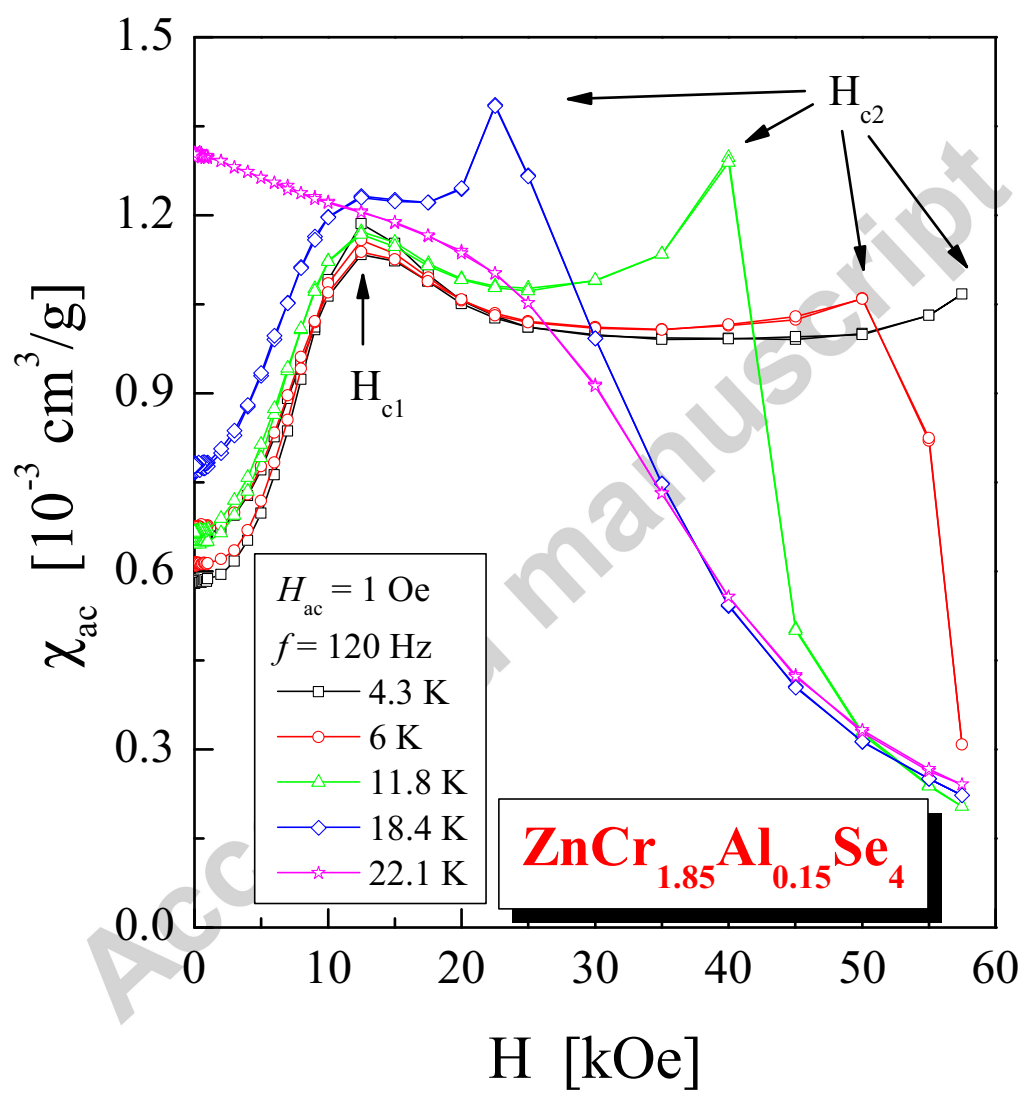
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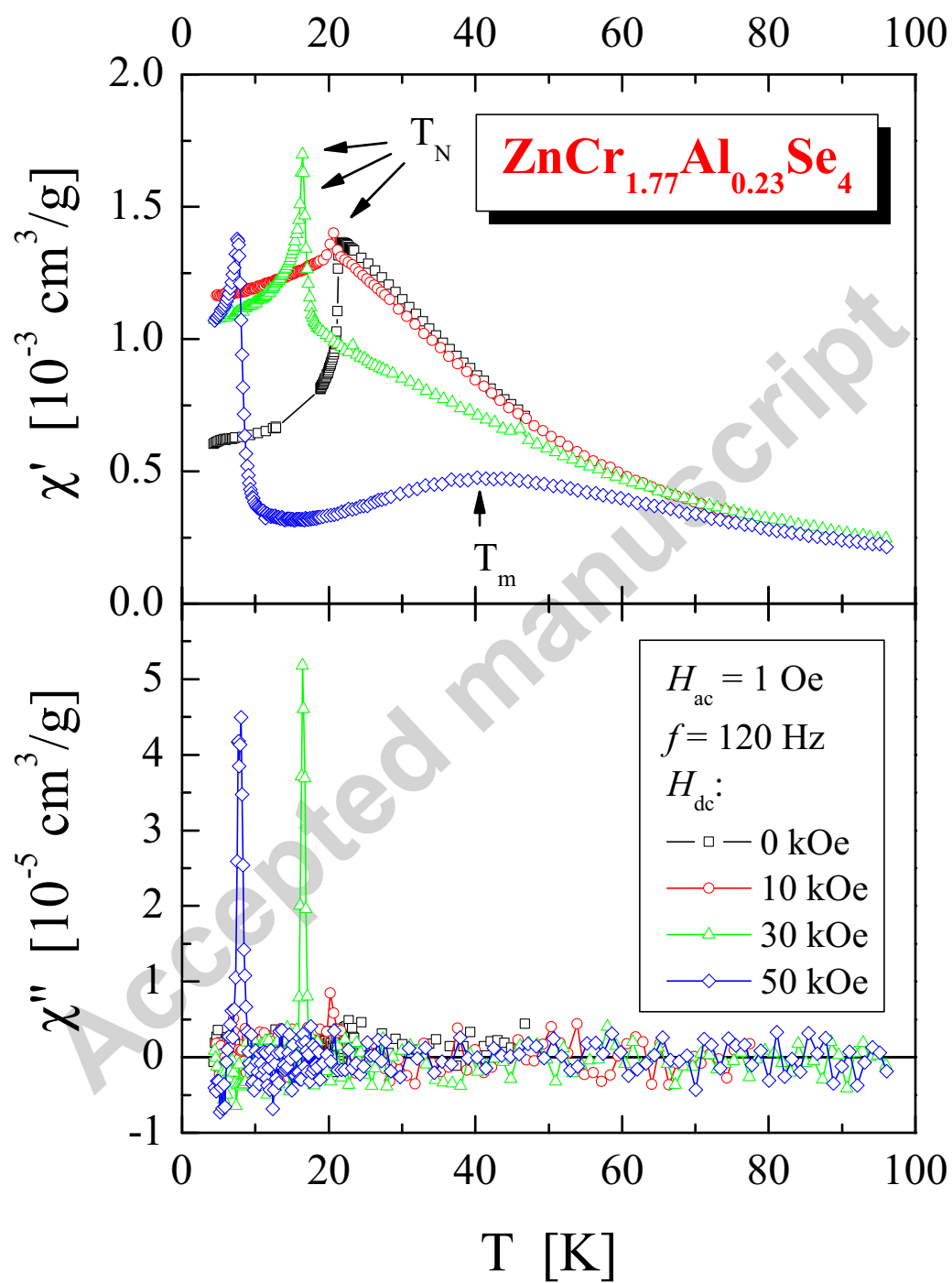


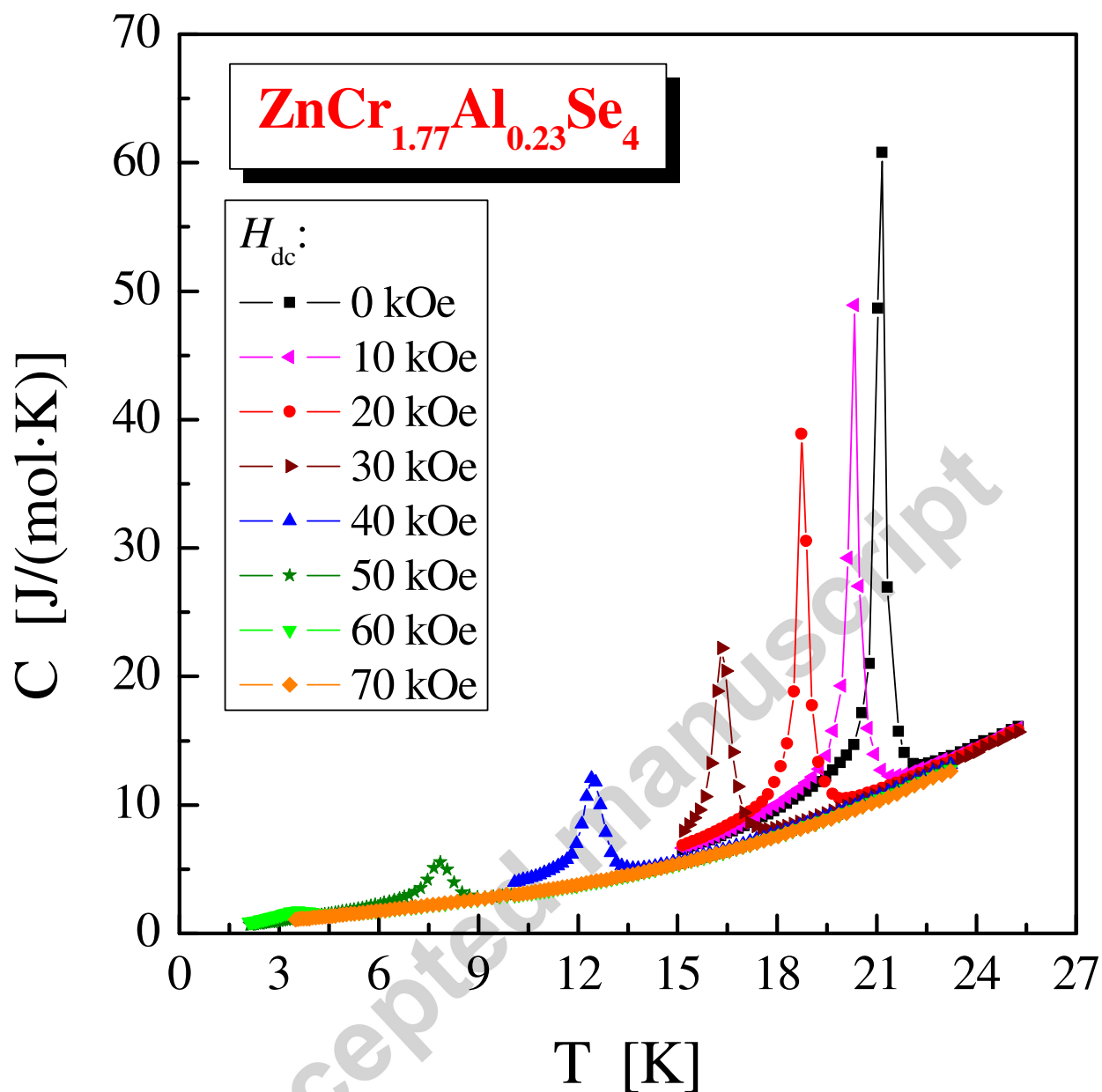




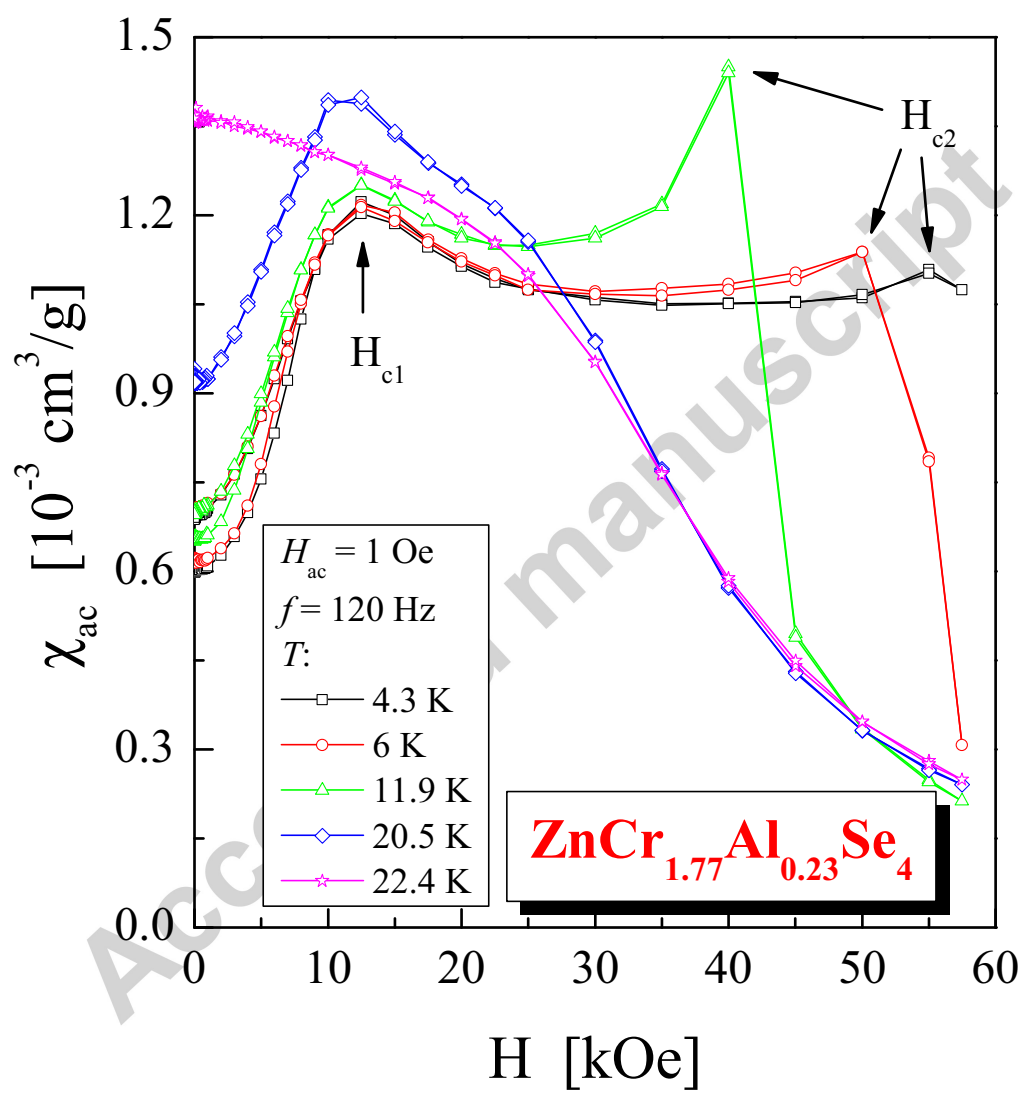


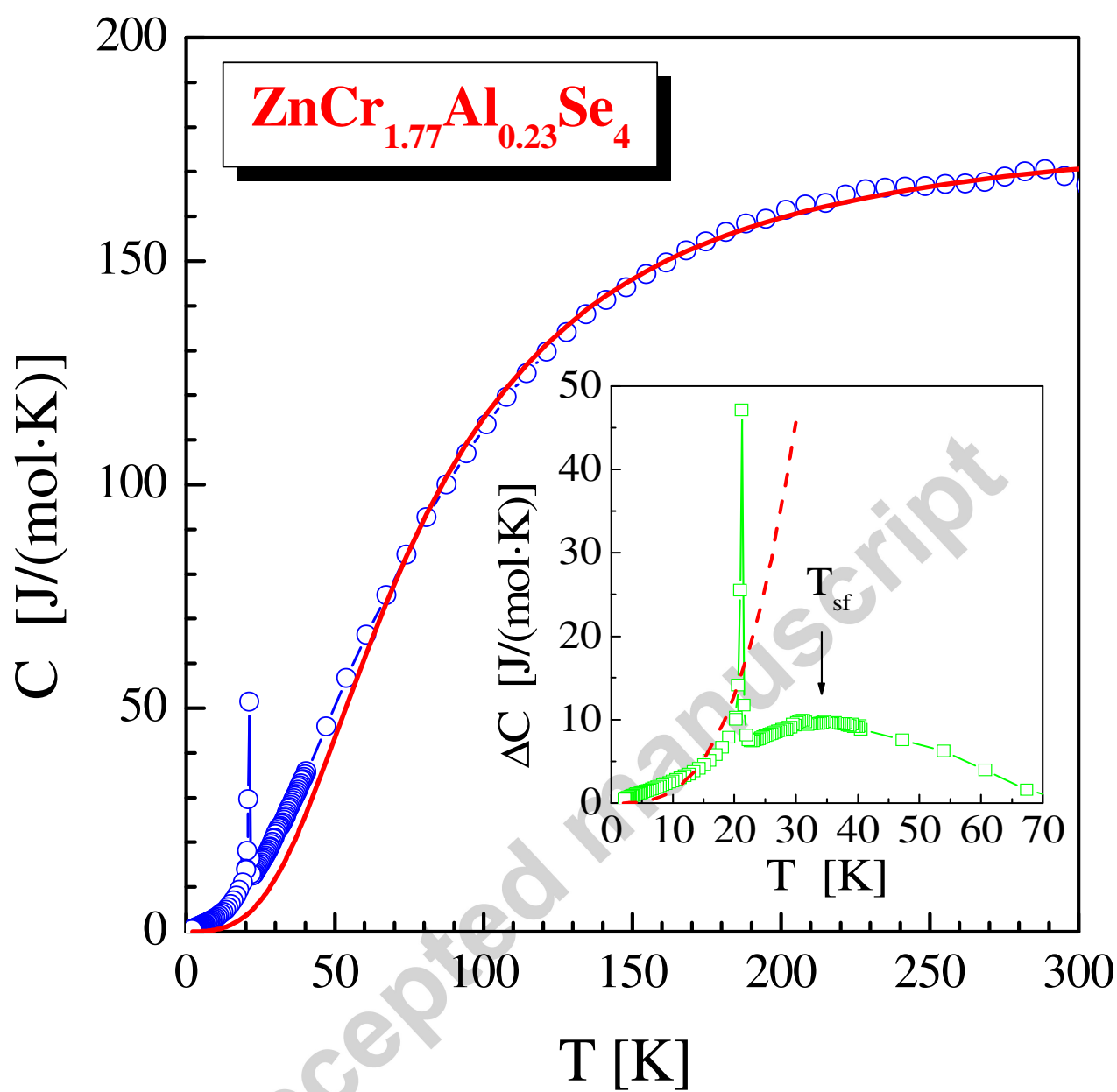


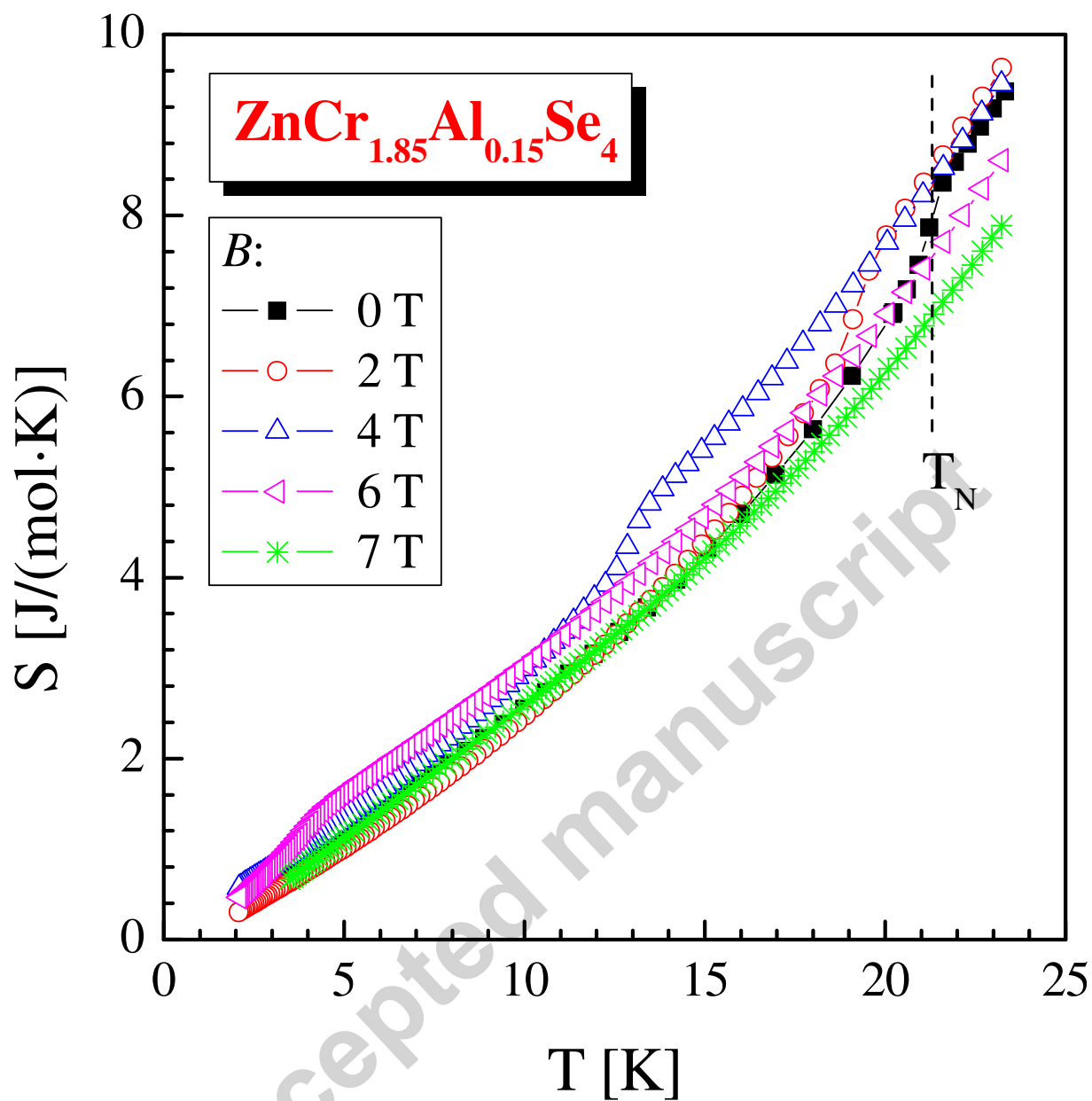


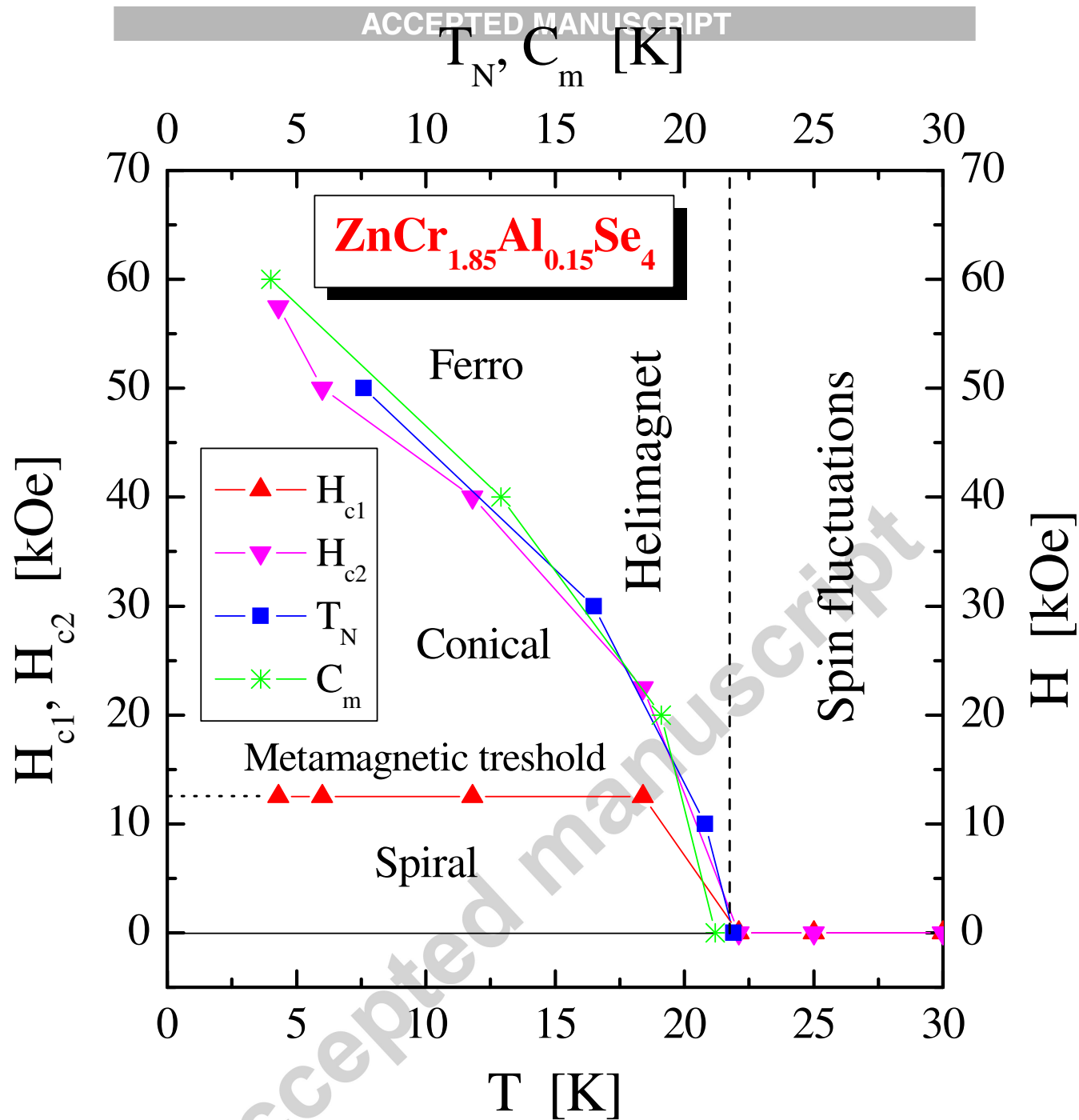


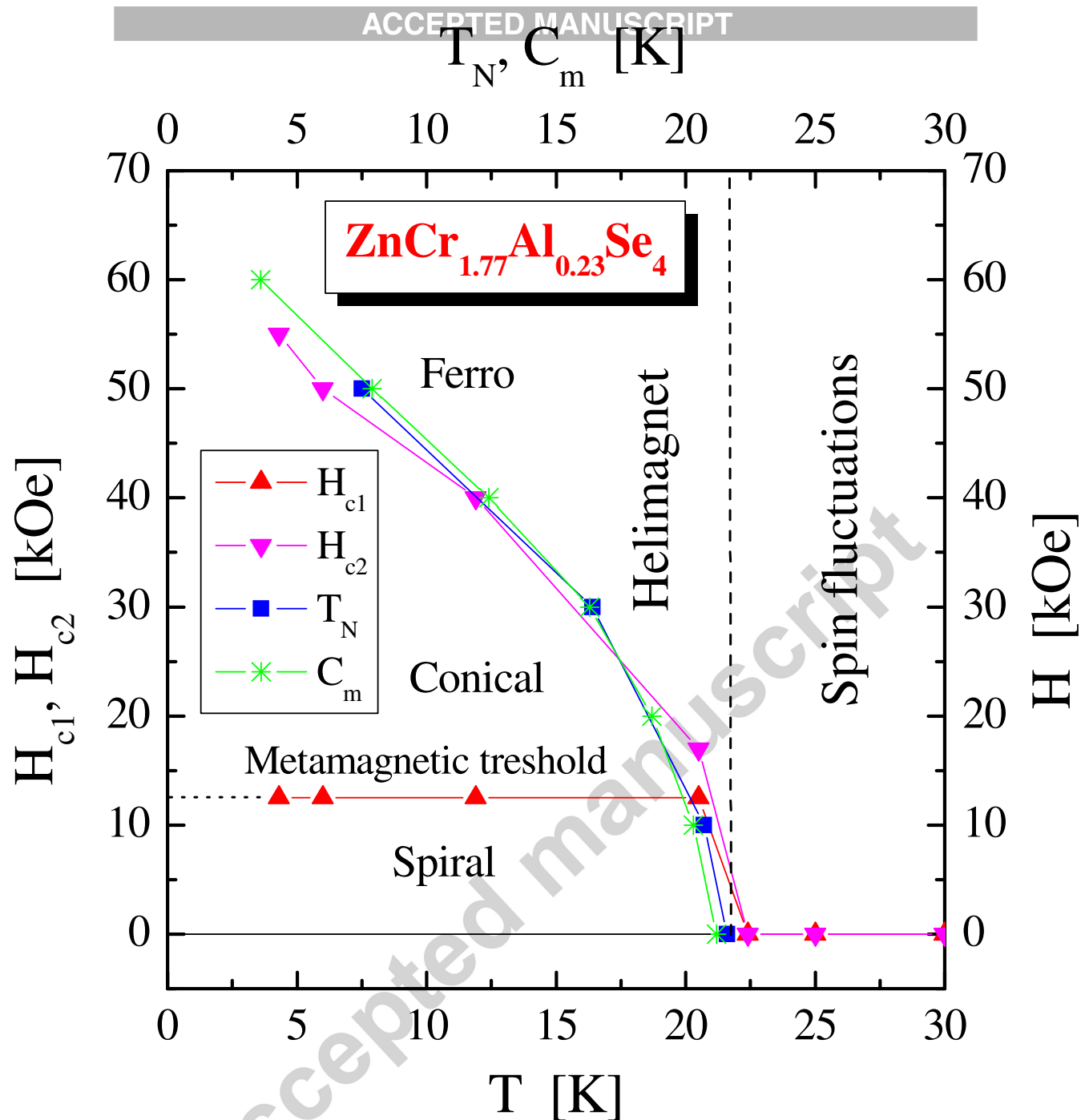












Specific heat,  $C_p$ , versus temperature  $T$  taken at different external magnetic fields for  $\text{ZnCr}_{1.77}\text{Al}_{0.23}\text{Se}_4$ . The specific heat peak is anomaly sharp for all magnetic fields and points towards a first-order transition in accordance with the structural transformation from cubic to tetragonal symmetry.

