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Critical Behaviour of the Mean-Field Ferromagnet $Cu_{1.02}[Cr_{1.77}Ti_{0.24}]Se_4$

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Magnetization, M, and susceptibility, χ, measurements showed both strong lowering of magnetic moment in comparison with $CuCr_2Se_4$ matrix and zero-field-cooling–field-cooling susceptibility splitting characteristic for the spin-glass behaviour. Isothermal magnetization curves, $M(H)$, easy saturate and large values both of the Curie $T_C = 253$ K and Curie–Weiss $\theta = 283.5$ K temperatures indicate the ferromagnetic order which coexists with the spin-glass state. The critical behaviour investigated around the paramagnetic–ferromagnetic phase transition revealed that the values of critical exponents are close to those predicted by the mean field model for long-range magnetic interactions.

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1. Introduction

$CuCr_2Se_4$ combines the p-type metallic and ferromagnetic properties with the Curie temperature $T_C = 416$ K and the Curie–Weiss temperature $\theta = 436$ K [1]. The chromium spins are coupled ferromagnetically via a double exchange interaction involving the electrons jumping between Cr^{3+} and Cr^{4+} ions [2, 3]. X-ray photoelectron spectroscopy and polarized neutron diffraction studies for $CuCr_2Se_4$ provide direct evidence for the presence of monovalent copper atoms with a $3d^{10}$ configuration [4, 5]. Various theoretical models of the critical phenomena, the mean-field, the three-dimensional (3D) Heisenberg, the 3D-Ising and the tricritical mean-field model used to explain the critical properties showed that the $CuCr_2Se_4$ was in best accordance with the 3D-Heisenberg model for which the critical exponents: $\beta = 0.37 \pm 0.02$, $\gamma = 1.32 \pm 0.02$ and $\delta = 4.2 \pm 0.3$ at $T_C = 417.20 \pm 0.05$ [6] are characteristic for short-range isotropic magnetic interactions.

The present contribution reports magnetic and critical properties for $Cu_{1.02}[Cr_{1.77}Ti_{0.24}]Se_4$. The anomalous lowering of the magnetic moment compared with $CuCr_2Se_4$ is discussed.

2. Experimental details

Polycrystalline $Cu_{1.02}[Cr_{1.77}Ti_{0.24}]Se_4$ sample was prepared by annealing stoichiometric mixtures of high purity ($\geq$ 99.99%) elements: Cu, Cr, Ti and Se. The mixtures were pulverized in agate mortar and sintered three times in evacuated quartz ampoules at temperature 1023 K for 14 days. The chemical composition of the polycrystalline selenospinel was determined using energy-dispersive X-ray spectrometry (EDXRF). The X-ray spectra from the sample were collected by thermoelectrically cooled Si-PIN detector (Amptek, USA) with resolution of 145 eV at 5.9 keV. The spinel under study have a normal cation distribution, the Cu ions being located at the tetrahedral sites, while the Cr and Ti ions at the octahedral ones. The unit cell parameter refined by the least squares method is $a = 1046.04$ pm. The critical exponents of $Cu_{1.02}[Cr_{1.77}Ti_{0.24}]Se_4$ were studied by measuring isothermal dc-magnetization around the paramagnetic–ferromagnetic (PM–FM) phase transition. Isothermal magnetization was measured with the aid of a Quantum Design System (MPMS XL) in the magnetic field up to 70 kOe and in the temperature range 230–260 K.

3. Results and discussion

The magnetic isotherm in Fig. 1 and the temperature dependences of molar susceptibility $\chi(T)$ and its reciprocal $1/\chi(T)$ as well as the magnetic parameters collected in Table show typical FM behaviour. The magnetic moment of 1.75 μ_B/f.u. is drastically lowered in comparison with the moment for $CuCr_2Se_4$. The increasing divergence between zero-field-cooling (ZFC) and field-cooling (FC) susceptibilities below T_C with reducing temperature suggests the coexistence of the FM order and SG state.

TABLE

Magnetic parameters for: (1) $CuCr_2Se_4$ matrix [1] and (2) $Cu_{1.02}Cr_{1.77}Ti_{0.24}Se_4$. C is the molar Curie constant, μ_{eff} is the effective magnetic moment, θ is the Curie–Weiss temperature, T_C is the Curie temperature taken from measurement, and M_S is the saturation magnetic moment per molecule at 2 K.

Spinel	C	μ_{eff} [μ_B/f.u.]	θ [K]	T_C [K]	M_S [μ_B/f.u.]
(1)	2.70	4.65	436	416	4.76
(2)	2.054	4.06	283.5	253	1.75

The critical behaviour of a magnetic system shows a second-order magnetic phase transition near T_C. It is characterized by the critical exponents β, γ and δ [7] defined from magnetization measurements as follows:

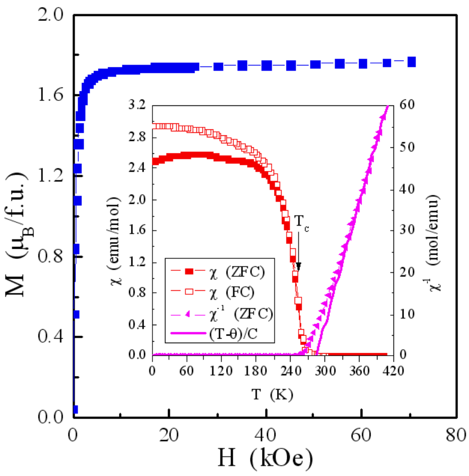

Fig. 1. Magnetization M vs. magnetic field H at 2 K. Inset: magnetic susceptibilities vs. temperature, χ and $1/\chi$ at $H = 200$ Oe. The solid (red) line $(T-\theta)/C$ indicates a Curie–Weiss behaviour. T_C is indicated by the arrow.

$$M_\mathrm{S}(T) = M_0|\varepsilon|^\beta, \quad \varepsilon < 0, \quad T < T_\mathrm{C}, \tag{1}$$

$$\chi_0^{-1}(T) = (h_0/M_0)\varepsilon^\gamma, \quad \varepsilon > 0, \quad T > T_\mathrm{C}, \tag{2}$$

$$M = DH^{1/\delta}, \quad \varepsilon = 0, \quad T = T_\mathrm{C}, \tag{3}$$

where ε is the reduced temperature $(T - T_\mathrm{C})/T_\mathrm{C}$, and M_0, h_0/M_0, and D are the critical amplitudes. The Curie temperature T_C defined as the temperature corresponding to the extreme $\mathrm{d}M/\mathrm{d}T$ (Table) is not very accurate, because it is dependent on the external magnetic field H. Therefore, the accurate $T_\mathrm{C}|_{\mathrm{H=0}}$ should be determined by the analysis of the critical exponents. For that purpose, the isothermal magnetization around T_C is measured, as gives Fig. 2, and the critical parameters (T_C, β, γ and δ) can be easily determined by analyzing the Arrott plot at temperature around T_C [8]. As in the Landau theory of phase transition, the magnetic equation of state for the condition of equilibrium is

$$H/M = 2a + 4bM^2, \tag{4}$$

where a and b are the coefficients temperature dependent [9]. Thus, the M^2 vs. H/M should appear as straight lines in the high-field range in the Arrott plot and the line at T_C should cross the origin. However, all curves in the Arrott plot, i.e. the isotherms of M^2 vs. H/M at temperatures around T_C (not shown here) are nonlinear even in the high-field region. Therefore, the modified Arrott plots were employed to obtain the correct β and γ according to the Arrott–Noakes equation of state [8]:

$$(H/M)^{1/\gamma} = \varepsilon + (M/M_1)^{1/\beta}, \tag{5}$$

where M_1 is the material constant.

The optimal values of β and γ were obtained by iterative approximation of isotherms on the modified Arrott plots (Fig. 3) when the isothermal curves become parallel straight lines (mean field values $\beta = 0.5$, $\gamma = 1$ give the regular Arrott plot M^2 vs. H/M). The slopes of the log–log plots (Fig. 4) yield values for β and γ, which are used to create a new modified Arrott plot and iterated until consistent. For the spinel under study, this procedure yields critical exponents $\beta = 0.5601$ and $\gamma = 1.2208$.

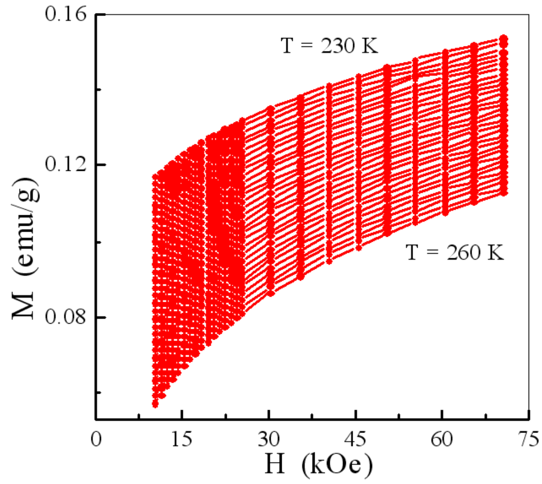

Fig. 2. Isothermal magnetization curves $M(H)$ around T_C.

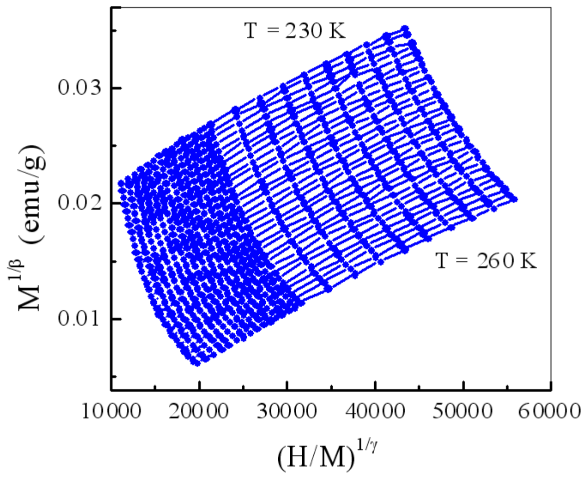

Fig. 3. Modified Arrott plot; $\beta = 0.5601$ and $\gamma = 1.2208$.

The third critical exponent δ is determined separately from the isothermal magnetization M vs. H at T_C [8] (Fig. 5). The values of the critical exponents characterizing the PM–FM transition are: $\beta = 0.5601$, $\gamma = 1.2208$ and $\delta = 3.1759$ at $T_\mathrm{C} = 257.5$ K. They are found to be consistent with the Widom scaling relation $\delta = 1 + \gamma/\beta$, implying the critical exponents are reliable. These values are close to the theoretical ones predicted by the mean-field model, characteristic for isotropic long-range exchange interactions ($\beta = 0.5$, $\gamma = 1$ and $\delta = 3$), whereas the critical exponents found for the $CuCr_2Se_4$ matrix were in best accordance with

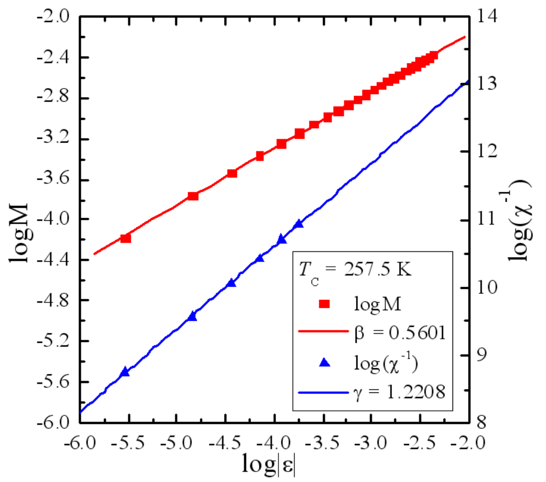

Fig. 4. $\log M$ vs. $\log|\varepsilon|$ with $T_C = 257.5$ K gives slope $\beta = 0.5601$ and $\log(\chi^{-1})$ vs. $\log|\varepsilon|$ gives slope $\gamma = 1.2208$.

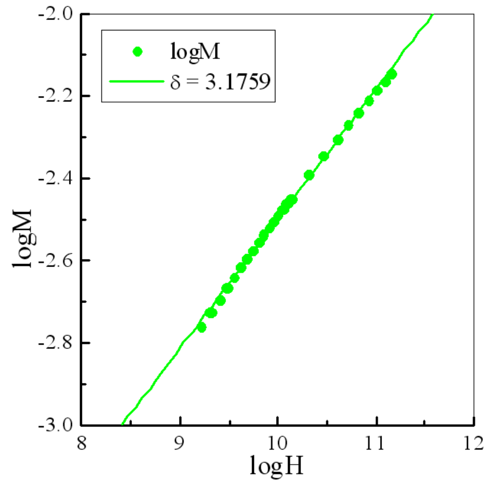

Fig. 5. $\log M$ vs. $\log H$ gives inverse slope $\delta = 3.1759$.

the 3D-Heisenberg model [6]. It means that the Ti-substitution strongly influences critical properties at T_C for $Cu_{1.02}[Cr_{1.77}Ti_{0.24}]Se_4$.

In the spinel under study a marked lowering of the saturation moment was noted when the magnetic Cr-sublattice was slightly disturbed, since Ti^{3+} ion carries the magnetic moment of 1.8 μ_B while Cr^{3+} one — 3.8 μ_B. Hypothetically, some of the moments may still be antiparallel or even perpendicular to the field, as in the $MnCr_2S_4$ [10]. However, the $CuCr_2Se_4$ matrix is fully saturated [1, 2]. Another possibility (caused both by elongation of the cation–anion distances in octahedral sites and/or the slight cation excess observed in this case) is the transition from a high (HS) to a low (LS) spin state in the $3d^3$ t_{2g} orbital of the chromium ions. Because in our case the lattice parameter of the spinel under study $a = 1046.04$ pm is slightly elongated in comparison to $a = 1033.5(3)$ pm of the parent $CuCr_2Se_4$ [11], the effect of electric charges associated with the surrounding ligands may lift the degeneracy of individual states [12], finally leading to the spin frustration and crossing of the HS and LS states.

4. Conclusions

Ti-substitution in $CuCr_2Se_4$ shifts the critical exponents from Heisenberg to the mean-field estimates. Such a shift is evidence of a crossover to isotropic long-range exchange interactions, affected by spin–lattice coupling, which correlates well with the spectacular reduction in magnetic moment.

Acknowledgments

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