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Magnetic properties of $CuCrZrSe_4$

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ABSTRACT

We report on structural and magnetic properties of the spinel compound $CuCrZrSe_4$. Rietveld refinement of the powder x-ray diffraction patterns reveals the normal spinel structure AB_2Se_4, where the Zr^{4+} and Cr^{3+} ions occupy the *B* sites, while the Cu^{1+} ions are located on *A* sites. The magnetic susceptibility reveals a Curie–Weiss law above 250 K with a ferromagnetic Curie–Weiss temperature $\theta_p = 115$ K and an effective paramagnetic moment $\mu_{eff} = 3.75\mu_B$ per Cr^{3+} ion corresponding to a *g* value $g=1.94$ in fair agreement with electron spin resonance (ESR) measurements. Below 100 K the magnetization deviates from the Curie–Weiss behaviour and splits into field-cooled (FC) and zero-field-cooled (ZFC) branches. A second anomaly in the magnetization close to 10 K, which is also visible in the ESR parameters, indicates the transition into a spin-glass state due to the random distribution of Zr and Cr ions on the *B* site. This is supported by the frequency dependence of the anomaly detected by AC susceptibility measurements.

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1. Introduction

Inorganic compounds with the AB_2X_4 spinel structure have been studied for many years and are in the focus of modern solid-state physics, because of their unusual physical properties, as there are heavy-fermion behaviour [1,2], complex spin order [3], spin dimerization [4,5], spin–orbital liquid [6,7], orbital glass [8], and multiferroicity [9–11]. These effects result from the interplay of spin, charge, orbital, and lattice degrees of freedom under the influence of strong magnetic frustration both from the geometric point of view as well as due to the bond structure [12–15]. In the crystallographic spinel structure, first solved by Bragg in 1915 [16], the cations occupy 1/8 of the tetrahedral (*A*) and 1/2 of the octahedral (*B*) voids within the face-centred cubic (fcc)-lattice formed by the X anions. Interesting physics arises, when the *B*-site cations become mixed in valence. As the cations show different site preferences, by choosing the appropriate atoms it is possible to realize a selective magnetic dilution in one of the two sublattices. The resulting magnetic properties have received a renewed attention from theoretical as well as experimental point of view, because these materials can exhibit spin-glass behaviour [17] and show a magneto-optical Kerr effect. Below a certain freezing temperature T_f, the spin-glass state arises from disorder due to dilution and underlying frustration of the magnetic interactions between the localized magnetic moments. The frustration may be due to competing ferromagnetic (*F*) and antiferromagnetic (*AF*) exchange interactions or result from purely topological effects, when the interactions are predominantly *AF*. In the pseudo-binary systems $CuCrS_2-MS_2$ ($M=Ti$, Sn), spinel phases of the composition $Cu_{2x}Cr_{2x}M_{2-2x}S_4$ have been discovered [18,19]. Their homogeneity range is wide: $0.68 \leq 2x \leq 1.26$ for $M=Ti$ and $0.2 \leq 2x \leq 1.36$ for $M=Sn$. For $2x=1$, the Cu^{1+} ions fully occupy the tetrahedral *A* sites, whereas the paramagnetic Cr^{3+} ions and the diamagnetic M^{4+} ions remain located on the *B* sites. X-ray diffraction did not show any ordering to occur between Cr^{3+} and M^{4+} ions. The experimental evidence, to date, indicates that the $Cu_{2x}Cr_{2x}M_{2-2x}S_4$ spinels are spin-glasses. These systems are very sensitive to the methods of preparation and deviations from stoichiometry [20]. This effect was discussed with respect to a deficiency and excess of cations in tetrahedral or octahedral voids of the spinel structure. In this series, when the stoichiometric composition is passed through as $2x$ increases, drastic changes occur in (i) the electric resistivity: the activation energy drops [18,19], (ii) magnetic susceptibility: the Curie–Weiss temperature θ_p changes from negative to positive values,

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which indicates that additional ferromagnetic couplings appear [18,19], and (iii) electron spin resonance (ESR): the line width passes through a maximum close to $x \sim 0.5$ and rapidly decreases for larger x, which suggests an enhancement of the exchange narrowing in the dense magnetic lattice [21]. Although there are numerous data available for powder materials, the studies of the effect of nonmagnetic Zr^{4+} substituted for Cr^{3+} atoms on the properties of the spinel structure are inconsistent. This raises the question about the proper location of the Zr ions and the metal excess of Cu in the spinel structure [22]. Recently the system $Cu(Cr_{1-x}Zr_x)_2S_4$ has been studied [23,24], where the Cu stoichiometry is kept unchanged. The substitution of Zr for Cr atoms has introduced antiferromagnetic interactions and spin frustration to the B sites resulting in a spin-glass state below $T_g \approx 10$ K. Above T_g the system exhibits a spin-liquid behaviour over a temperature range of $T_g \leq T \leq \theta_p$ limited by the Curie–Weiss temperature, which ranges from $\theta_p = 219$ K for $x = 0.4$ to $\theta_p = 24$ K for $x = 0.55$. In the present paper we focus on the corresponding selenide compound $CuCrZrSe_4$ to study the influence of the larger Se anions on the crystallographic and magnetic properties.

2. Experimental

Polycrystalline $CuCrZrSe_4$ has been prepared by solid-state reaction from the stoichiometric mixture of the pure elements as described previously [25,26]. Room-temperature powder x-ray diffraction (XRD) measurements were carried out with a STOE STAD-IP diffractometer in the Bragg–Brentano geometry using CuKα radiation ($\lambda = 1.54059$ Å). The XRD patterns were recorded from angles $2\theta = 10-130^\circ$ with a 0.02° step size. Further analysis was carried out by the Rietveld method using the FULLPROF program [27]. The magnetic properties of the powder sample were studied in the temperature interval from 2 to 400 K using a commercial superconducting quantum interference device (SQUID) magnetometer “MPMS 5” from Quantum Design. Electron spin resonance (ESR) experiments were performed in a Bruker ELEXSYS E500-CW spectrometer at X-band frequency ($f = 9.36$ GHz), equipped with a continuous He-gas flow cryostat (Oxford Instruments) working in the temperature range from liquid helium to room temperature.

3. Results and discussion

3.1. Powder x-ray diffraction

Powder x-ray diffraction studies prove the proper normal spinel phase, which could be indexed satisfactorily based on a cubic cell (space group $Fd\overline{3}m$) with the lattice parameter $a = 10.649(2)$ Å in agreement with Ref. [28]. Fig. 1 shows the XRD patterns of $CuCrZrSe_4$, Table 1 gives the crystallographic data and the structure refinement. The Rietveld refinement was started by using the structural model of $MnSc_2S_4$ and the lattice parameter obtained with the program DICVOL04 [29]. The origin of the unit cell was taken at the point $\overline{3}m$ of the space group $Fd\overline{3}m$ (*No*227 in the International Tables for x-ray Crystallography) with Se in 32*e*, the tetrahedral site in 8*a* and the octahedral site in 16*d*. The refinement of 14 parameters (zero shift, scale factor, asymmetry parameter, and mixing parameter of the pseudo-Voigt peak shape function, unit-cell parameter, positional parameters, and isotropic temperature factor) converged to the final profile yielding agreement factors of $R_B = 0.116$, $R_p = 0.339$, and $R_{wp} = 0.232$. These factor values are fairly large indicating probably a strong local variation of the Cr:Zr ratio. Nevertheless, the difference spectrum shows a good agreement between observed and calculated spectrum. Thus, as documented in Table 2, the Rietveld refinement showed that in the sample under study the Cu^{1+} ions were exclusively located on the tetrahedral position 8*a*: (1/8, 1/8, 1/8), while the Zr^{4+} and Cr^{3+} ions randomly share the octahedral position 16*d*: (1/2, 1/2, 1/2) in the spinel structure. A remarkable structural fact concerns the absence of any deformation of the octahedral and tetrahedral sites. No sign of any structural ordering of the Cr and Zr ions is observed.

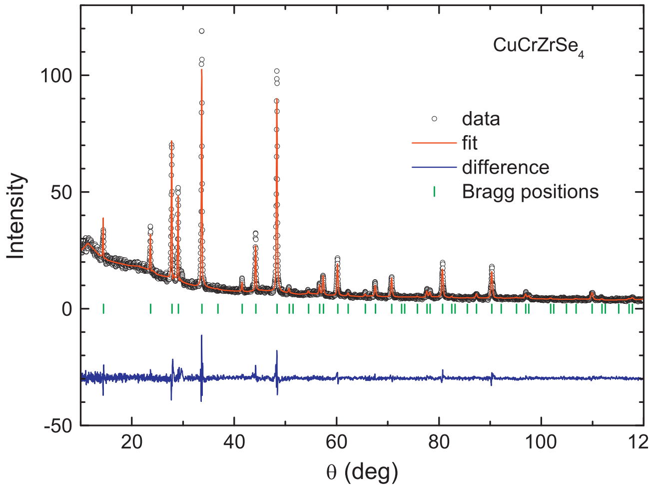

Fig. 1. Observed and fitted x-ray diffraction profiles of $CuCrZrSe_4$ at 300 K. The lower line indicates the difference between observed and calculated intensities and the vertical bars indicate the calculated peak positions.

Table 1
Crystal data and experimental details of the x-ray structure refinement.

Empirical formula	$CuCrZrSe_4$
Crystal data	
Crystal system	Cubic
Space group	$Fd\overline{3}m$
a (Å)	10.649(2)
Number of atom per asymmetrical unit	$Z = 8$
Density calc. (g/m^3)	0.8484
Data collection	
Radiation, wavelength (Å)	CuKα_1, CuKα_2
2θ range (°)	10
Temperature	300 K
Counting	0.02°
Refinement	
Type of profiles function	Pseudo-Voigt
Number of refined parameters	14
Final R_B	0.116
Final R_p	0.339
Final R_{wp}	0.232

Table 2
Positions, occupancies, and thermal parameters for $CuCrZrSe_4$.

Atom	X	Y	Z	B_{iso} (Å^2)	Occupancy
Cu	0.125	0.125	0.125	0.753	0.080
Cr	0.500	0.500	0.500	1.583	0.080
Zr	0.500	0.500	0.500	1.583	0.080
Se	0.254	0.254	0.254	1.032	0.320

3.2. Magnetic properties

Fig. 2 shows the temperature dependence of the magnetic susceptibility $\chi = M/H$ of $CuCrZrSe_4$ derived from the magnetization

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