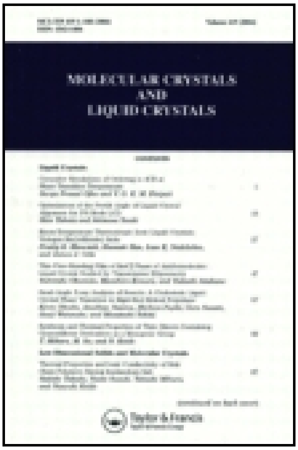

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Susceptibility of Deintercalated Tunnel Compound of $K_xCr_5Se_8$ and Mössbauer Spectra of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$

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To cite this article: Tsukio Ohtani, Shuji Kawasaki, Mikio Takano, Yoshiaki Harima, Takashi Chika & Shuichi Kirino (2000): Magnetic Susceptibility of Deintercalated Tunnel Compound of $K_xCr_5Se_8$ and Mössbauer Spectra of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 39-44

To link to this article: http://dx.doi.org/10.1080/10587250008026114

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 39-44
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Printed in Malaysia

Magnetic Susceptibility of Deintercalated Tunnel Compound of $K_xCr_5Se_8$ and Mössbauer Spectra of $K_x(Cr_{0.95}\,{}^{57}Fe_{0.05})_5Se_8$

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KCr_5Se_8 has a TlV_5S_8-type structure, containing K ions in one-dimensional tunnels. Deintercalated samples of $K_xCr_5Se_8$ ($0.32 \leq x \leq 0.93$) were prepared by leaching method using $AlCl_3/FeCl_3$ aqueous solution. These samples showed a broad peak of magnetic susceptibility at ca.130 K. ^{57}Fe-Mössbauer spectra of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ ($x = 1.0, 0.49$) showed a quadrupole doublet at 300 K. Magnetic sextets appeared at 4.2 K in both samples, indicative of magnetic ordering. The observed isomer shift indicated that the charge of Fe is +3 in both samples. It was proposed that Se^{2-} was partially oxidized by the deintercalation.

Keywords: KCr_5Se_8; tunnel compound; deintercalation; magnetic susceptibility; antiferromagnetism; Mössbauer spectroscopy

INTRODUCTION

KCr_5Se_8[1] has a TlV_5S_8 type structure (space group $C2/m$)[2]. The structure of KCr_5Se_8 is characterized by a hollandite-like $[Cr_5Se_8]$ framework, which is built up of edge and face sharing $CrSe_6$ octahedra forming large tunnels running parallel to the *b* axis. K ions are intercalated within these tunnels. Shöllhorn and coworkers deintercalated Tl ions from TlV_5S_8 using electrochemical method[3]. They found that the lower limit of x was 0.33 for $Tl_xV_5S_8$, and suggested that Tl^+ is oxidized to Tl^{3+} during the reaction, the charge of the host lattice remaining constant. Ohtani *et al.* also prepared deintercalated samples of $Tl_xV_5S_8$ ($0.33 \leq$

$x < 1.0$)[4], $Tl_xV_5Se_8$ ($0.33 \leq x < 1.0$)[1], and $Tl_xCr_5Se_8$ ($0.33 \leq x < 1.0$)[5] by leaching method using $AlCl_3/FeCl_3$ aqueous solution. They found that $TlCr_5Se_8$ and $Tl_{0.65}Cr_5Se_8$ show a Néel like cusp of magnetic susceptibility, χ at 52 K, and that $Tl_{0.33}Cr_5Se_8$ a broad peak of χ at ca. 100 K[5]. The effective magnetic moment of these samples was close to that of Cr^{3+}, invariable with the Tl content. On the other hand, Bensch *et al.* prepared $Tl_xCr_5Se_8$ ($0 \leq x < 1.0$) using Br_2/CH_3CN solution[6]. On the basis of X-ray diffraction measurements, they argued that the charge of Tl ions is not variable during the reaction, but Cr^{3+} partially changes to Cr^{4+}. In the present study we performed χ measurements for $K_xCr_5Se_8$ ($0.32 \leq x \leq 0.98$), which were obtained by the leaching method. In order to obtain the more detailed information on the magnetic properties, ^{57}Fe-Mössbauer measurements were performed on ^{57}Fe doped samples.

EXPERIMENTS

Samples of $K_{1.0}Cr_5Se_8$ and $K_{1.0}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ were prepared as follows. The elemental mixtures with desired ratio were heated at 800°C for 2 weeks in evacuated silica tubes. The products were annealed at 800°C for 1 week after pelletizing. ^{57}Fe was obtained by H_2 reduction of $^{57}Fe_2O_3$. K atoms in these samples were deintercalated using $AlCl_3/FeCl_3$ aqueous solution (for details see refs. [1], [4] and [5]). Deintercalated samples were not prepared by heating the elements. The chemical compositions were analyzed by EPMA (electron probe microanalyzer). Magnetic susceptibility was measured by using a Faraday type torsion balance from 77 to 273 K. ^{57}Fe-Mössbauer spectra were obtained for ^{57}Fe doped samples at 300, 77, and 4.2 K using a ^{57}Co/Rh γ-ray source. The source velocity (V) was calibrated by using pure iron metal as a control material.

RESULTS AND DISCUSSION

$K_xCr_5Se_8$ ($0.32 \le x \le 0.98$)

The lower limit of x in $K_xCr_5Se_8$ were observed to be 0.32. Fig. 1 gives lattice parameters of $K_xCr_5Se_8$ as a function of x. Lattice parameters continuously decreased with decreasing x. Since the tunnels run along the b axis, it is reasonable that values of both a and c decreased with decreasing x. The other isotypic compounds did not show the decrease of b during the deintercalation[1,4-6], contrary to the present results. The reason of this discrepancy is not clear.

Fig. 2 shows temperature

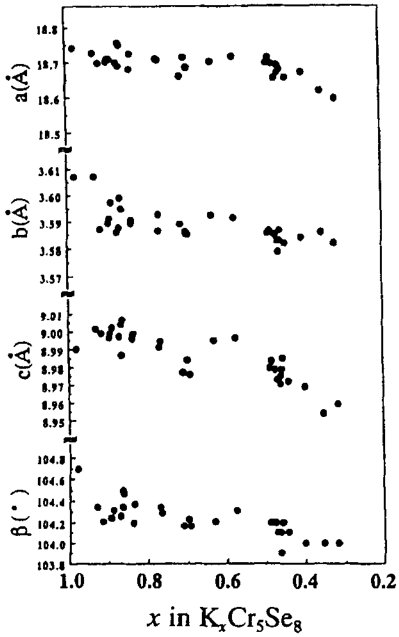

FIGURE 1 Lattice constants of $K_xCr_5Se_8$.

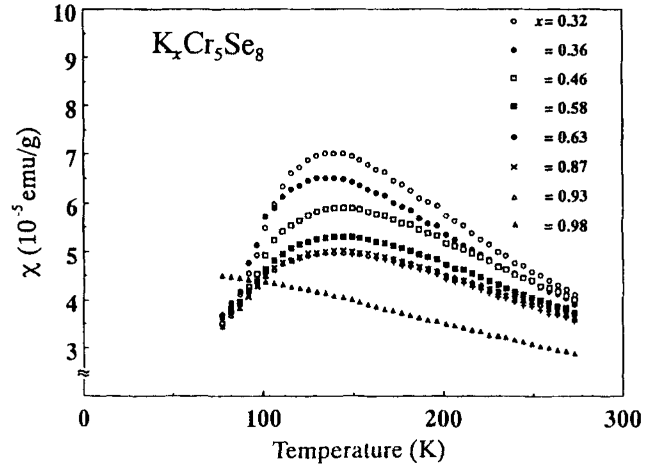

FIGURE 2 Temperature variations of magnetic susceptibility of $K_xCr_5Se_8$.

dependences of χ for powdered samples of $K_xCr_5Se_8$. $K_{0.98}Cr_5Se_8$ shows a continuous χ -*T* curve, being slightly concave downwards. $K_{0.98}Cr_5Se_8$ is supposed to exhibit a Néel point at lower temperature below 77 K, as was observed in $TlCr_5Se_8$ at 52 K[5]. The samples of $x \leq 0.93$ showed a broad peak of χ at ca. 130 K, almost invariable with *x*. The peak of χ would correspond to the Néel point. The broadness of the peak may be due to the inhomogeneous distribution of K ions, originating from that the samples were not annealed after the deintercalation. Since the χ -*T* curves did not obey the Curie-Weiss law, we can not discuss the magnetic properties more extensively.

χ of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$

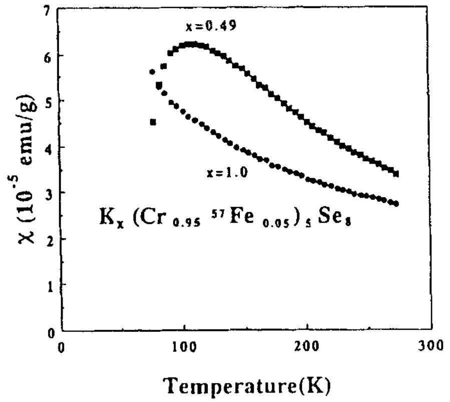

FIGURE 3 Temperature variations of χ of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ (x = 0.45, 1.0).

Fig. 3 shows temperature variations of χ of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ (x =0.49, 1.0). The behaviors are substantially identical with those of $K_xCr_5Se_8$, except that the peak temperature is lowered to ca. 100K for $K_{0.49}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$. The χ -*T* curve of $K_{1.0}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ obeyed the Curie-Weiss law. The Weiss temperature θ was – 92K, indicative of antiferromagnetic interaction. The effective magnetic moment P_{eff} was $3.58\mu_B/(Cr_{0.95}Fe_{0.05})$, which is close to the spin-only value of Cr^{3+} ($=3.87\mu_B$). The χ values of $K_{0.49}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ did not obey the Curie-Weiss law even above 100 K.

Mössbauer spectra

Figs. 4 (a) and 4 (b) show Mössbauer spectra observed at 300, 77, and 4.2 K for

$K_{1.0}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ and $K_{0.49}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$, respectively. Table I gives hyperfine parameters determined by fitting to Lorenzian lines. Both samples showed a quadrupole doublet at 300 K. The value of isomer shift δ was 0.52 mm/s for both samples, which is comparable with the published value for Fe^{3+} in e.g. $Y_3Fe_5O_{12}$[7]. This indicates that Fe^{3+} was not oxidized to Fe^{4+} during the deintercalation reaction. Mössbauer spectra give no information on the charge of Cr ions. But, Cr^{4+} is an unusual valent state. It is more reasonable, thus, to consider that a part of Se^{2-} ions, rather than Cr^{3+} ions, are oxidized by the deintercalation of K^+. Both samples showed magnetic sextets at low temperatures. In Mössbauer measurements, doped ^{57}Fe atoms have been used as the probes for observ-

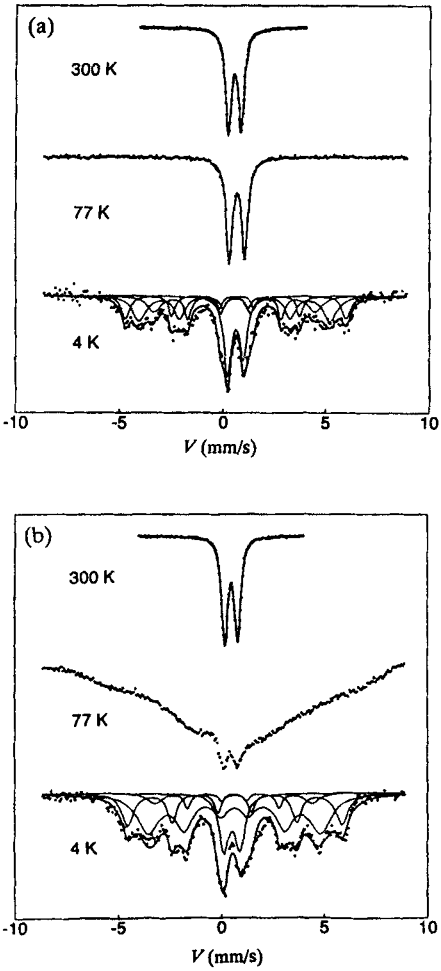

FIGURE 4 Mössbauer spectra of $K_{1.0}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ (a), and $K_{0.49}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ (b). Solid lines are computed spectra. The velocity scale was calibrated against pure iron metal.

TABLE I Isomer shift *IS*, hyperfine field *HF*, quadrupole splitting *QS*, full peak width at the half maximum Γ, and relative intensity *I* of ^{57}Fe-Mössbauer spectra of $K_x(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$ (x = 1.0, 0.49).

T(K)	*IS*(mm/s)	*HF*(kOe)	*QS*(mm/s)	Γ(mm/s)	*I*(%)
		$K_{1.0}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$			
300	0.52	0	0.63	0.35	100
77	0.65	0	0.76	0.37	100
4	0.62	0	0.78	0.45	26
	0.58	241	0	0.52	22
	0.60	287	0	0.60	33
	0.65	332	0	0.38	19
		$K_{0.49}(Cr_{0.95}{}^{57}Fe_{0.05})_5Se_8$			
300	0.52	0	0.63	0.35	100
77	-	-	-	-	-
4	0.54	0	0.79	0.45	17
	0.63	237	0	0.52	9
	0.66	260	0	0.80	50
	0.67	323	0	0.54	24

ing the magnetic properties of the host matrix[8]. It is, thus, considered that both the present samples exhibit the magnetic ordering at low temperatures. The almost identical parameters of both samples imply that the magnetic nature is invariable with the deintercalation. The ordering temperature of the $K_{0.49}$ sample is higher than that of the $K_{1.0}$ sample. These results are compatible with the χ data. The spectra observed at 4.2 K showed the superposition of one doublet and at least three sextets for both samples. The reason of the coexistence is not clear yet. The more detailed investigations such as neutron diffraction measurements should be needed to clarify the magnetic structures.

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