

## Strongly correlated behavior in magnetoresistive $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ spinels

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Structural and thermodynamic properties of the spinel-type colossal magnetoresistance (CMR) system  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  ( $0 \leq x \leq 0.3$ ) have been investigated. Synchrotron x-ray powder diffraction measurements on  $x=0.2$  reveal significant changes in the lattice at the Curie temperature  $T_c$ , which bear a close resemblance to those of perovskite manganites exhibiting CMR. The heat capacity  $C_p$  shows that the stoichiometric  $\text{FeCr}_2\text{S}_4$  undergoes an orbital ordering at 9.6 K induced by the dynamic-to-static Jahn-Teller (JT) distortion, which results in the opening of a spin gap. For  $x \geq 0.2$  the JT distortion remains dynamic at all temperatures, and the low-temperature  $C_p$  contains the  $T^{3/2}$  term due to ferrimagnetic spin waves. These results suggest that  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  represents another class of strongly correlated CMR materials where charge, spin, and lattice degrees of freedom are intimately interrelated.

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The physics of colossal magnetoresistance (CMR) in mixed-valence perovskite manganites, such as  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A}=\text{Ca}, \text{Sr}, \text{or Ba}$ ), has been the subject of considerable interest in recent years.<sup>1,2</sup> The fascinating properties exhibited by these systems are recognized today as one aspect of strongly correlated electron systems, where interplay among different degrees of freedom become prominent and even small perturbations can result in significant changes in physical properties.<sup>3</sup> The stoichiometric  $\text{LaMnO}_3$  is an antiferromagnetic insulator with a cooperative Jahn-Teller (JT) distortion of the  $\text{Mn}^{3+}\text{O}_6$  octahedra below  $T_{\text{JT}} \sim 750$  K. The resulting in-plane orbital order induces strong anisotropic spin interactions, as evidenced by the layered antiferromagnetic structure. For the doping level of  $x \sim 0.2-0.4$ , the static JT distortion disappears, and these materials show a ferromagnetic transition that is accompanied by a sharp drop in resistivity. The intimate connection between magnetic order and electrical transport is generally explained with the double exchange (DE) mechanism, in which electron hopping between  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions mediate ferromagnetic interactions. Consequently, the application of magnetic field results in suppressing the spin disorder and raising the transition temperature  $T_c$ , leading to the CMR effect. However, the DE mechanism alone is not sufficient to quantitatively explain the CMR,<sup>4</sup> and a strong electron-phonon coupling due to dynamic JT distortion is also believed to be important. Indeed, the polaron conductivity for  $T > T_c$  (Ref. 2) and significant changes in the structural properties at  $T_c$  (Refs. 5 and 6) have been recognized as the hallmark of strong interplay among charge, spin, and lattice degrees of freedom.

On the other hand, subsequent discoveries of CMR in other systems have established that neither DE nor lattice polarons are essential for obtaining CMR. In pyrochlore  $\text{Tl}_2\text{Mn}_2\text{O}_7$ , for example, there is no JT-active  $\text{Mn}^{3+}$  and the system shows a negligible lattice response at  $T_c$ .<sup>7,8</sup> The CMR appears to result from strong scattering of charge carriers by spin fluctuations associated with the ferromagnetic ordering.<sup>7,8</sup> A similar spin-fluctuation scenario seems to be operative in a wide variety of doped magnetic semiconductors exhibiting large magnetoresistive effects,<sup>9</sup> including Eu

chalcogenides and spinel  $\text{CdCr}_2\text{Se}_4$ . In these classes of materials, one-electron band theories can correctly predict the ground states,<sup>10</sup> and correlation effects are not expected to play a major role. The situation is not as clear for spinel  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ , however, which exhibits CMR associated with ferrimagnetic ordering of the Fe and Cr sublattices.<sup>11</sup> Though  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  is structurally and chemically similar to  $\text{CdCr}_2\text{Se}_4$ , there are a number of features that distinguish the system from other magnetic semiconductors and, perhaps, resemble those of the perovskite manganites.

The parent compound  $\text{FeCr}_2\text{S}_4$  is a single-valence semiconductor with  $T_c \sim 170$  K and the saturation moment of  $\sim 1.5\mu_B$ . The  $\text{Fe}^{2+}$  ion in the tetrahedral A site of the spinel  $\text{AB}_2\text{X}_4$  has the electronic configuration of  $e_g^3 t_{2g}^3$ , with the degenerate  $e_g$  orbitals. The orbital degeneracy leads to orbital ordering below 10 K, in the form of a dynamic-to-static JT transition.<sup>12,13</sup> The  $\text{Cr}^{3+}$  ion in the octahedral B site has the electronic configuration of  $t_{2g}^3$ , and is JT inactive. The band-structure calculations<sup>14</sup> showed the importance of electron correlations in obtaining the insulating and orbital-ordered ground state. In  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  ( $0 \leq x \leq 0.5$ ), Cu substitutes the Fe site in the monovalent state,<sup>15</sup> which results in the depopulation of the narrow Fe-derived band<sup>15</sup> and the formation of JT-inactive  $\text{Fe}^{3+}$ . Although both  $T_c$  and the saturation moment increase monotonously with  $x$ , the resistivity  $\rho$  shows nonmonotonic behavior, showing significant reduction up to  $x \sim 0.2$ , above which  $\rho$  increases.<sup>15</sup> At  $x=0.5$ , all the Fe ions are in the trivalent state, and further increase in  $x$  results in insulator-to-metal transition.<sup>15</sup> The  $x=1$  member  $\text{CuCr}_2\text{S}_4$  orders ferromagnetically at  $\sim 420$  K, and is believed to be a half metal.<sup>14,16</sup> The temperature  $T$  dependence of  $\rho$  shows qualitatively similar behavior for  $0 \leq x \leq 0.5$ , where  $\rho$  changes from semiconducting above  $T_c$  to metalliclike ( $d\rho/dT > 0$ ) below  $T_c$ , resulting in the CMR. At  $T \ll T_c$ ,  $\rho$  again shows semiconducting behavior. To explain the CMR, Palmer and Greaves<sup>17</sup> have recently proposed a model where an antiferromagnetic exchange on the three centers of Fe-Cr-Fe provides facile transfer of the minority  $\text{Fe}^{2+} e_g$  electrons via Cr  $e_g$  levels. This model, dubbed “triple exchange,” also explains the  $x$  dependence of  $\rho$  (Ref. 18) and

invokes the importance of mixed-valence hopping conductivity for  $T > T_c$ . However, previous studies have mostly been directed at measurements of charge and magnetic response, and there have been little experimental efforts to probe the orbital and lattice degrees of freedom, which are known to be important in the case of perovskites. In this paper, we present detailed structural and thermodynamic studies on  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ , which demonstrate the strong coupling between magnetism, transport, and structure in  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ , thereby providing opportunities to explore the interplay among different degrees of freedom in another class of strongly correlated CMR systems.

Polycrystalline samples of  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  ( $x=0, 0.1, 0.2$ , and  $0.3$ ) were prepared by solid-state reactions of the elements in evacuated quartz tubes. For  $0.1 \leq x \leq 0.3$ , stoichiometric amounts of starting materials were used. For  $x=0$ , three samples with the starting composition ratio of Fe/Cr=1.00/2.00 (sample A), 0.99/2.01 (sample B), and 0.97/2.03 (sample C) were prepared. Powder x-ray diffraction showed that the sample C contains a small amount ( $\sim 3\%$ ) of  $\text{Cr}_2\text{S}_3$ , presumably due to the excess Cr. All the other samples were single phase. Synchrotron x-ray powder diffraction data were collected at the BL02B2 beamline of SPring-8 at various  $T$  between 100 and 400 K, using a wavelength of 0.413 299 Å. Structural parameters were refined by the Rietveld method, using the program RIETAN-2000.<sup>19</sup> Heat capacity  $C_p$  was measured by a relaxation method using a Quantum Design PPMS. Magnetization  $M$  was obtained with a commercial superconducting quantum interference device (SQUID) magnetometer. Electrical resistivity  $\rho$  was measured with a standard four-probe technique. The  $M$  and  $\rho$  data for each composition were fully consistent with the reported values.

In Fig. 1(a) we show the  $T$  dependence of  $\rho$  and  $M$  for  $x=0.2$ , the concentration where  $\rho$  is minimized for the region  $0 \leq x \leq 0.5$ .<sup>15</sup> As a signature of the CMR system, the onset of ferrimagnetic order ( $T_c=249$  K) induces a strong drop in  $\rho$ . The  $T$  dependence of the cubic lattice parameter  $a$  is shown in Fig. 1(b).<sup>20</sup> From 400 to 260 K,  $a$  contracts linearly with decreasing  $T$  by  $\sim 0.1\%$ . At  $T_c$ , there is a significant lattice contraction and  $a$  acquires a pronounced  $T$  dependence, indicating a strong coupling between the lattice and magnetism. Similar behavior in the abrupt reduction of the lattice parameter at  $T_c$  is observed in the CMR perovskites,<sup>5,6</sup> and is consistent with the formation of stronger metalliclike bonds in the magnetically ordered state. It should be noted that, aside from the perovskites, other CMR systems do *not* generally show such a behavior in lattice at  $T_c$ . As mentioned above,  $\text{Ti}_2\text{Mn}_2\text{O}_7$  shows negligible change in the lattice at  $T_c$ .<sup>7,8</sup> Although some magnetostriction is observed in  $\text{CdCr}_2\text{Se}_4$ ,<sup>21</sup> the extrapolation of the high- $T$  ( $T > T_c$ )  $a$  lies below that of the low- $T$  ferromagnetic state, which is opposite to what is observed for  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  and the perovskites. In the perovskites, the large reduction in the lattice parameter at  $T_c$  is attributed to a decrease in the incoherent JT distortions of the oxygen octahedra around  $\text{Mn}^{3+}$ .<sup>5,6</sup> This view is strongly supported by the observation of an abrupt reduction of the oxygen Debye-Waller factor at  $T_c$  on cooling.<sup>5,6</sup> To examine whether similar behavior is observed in  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ , we show in Fig. 1(c) the  $T$  dependence of

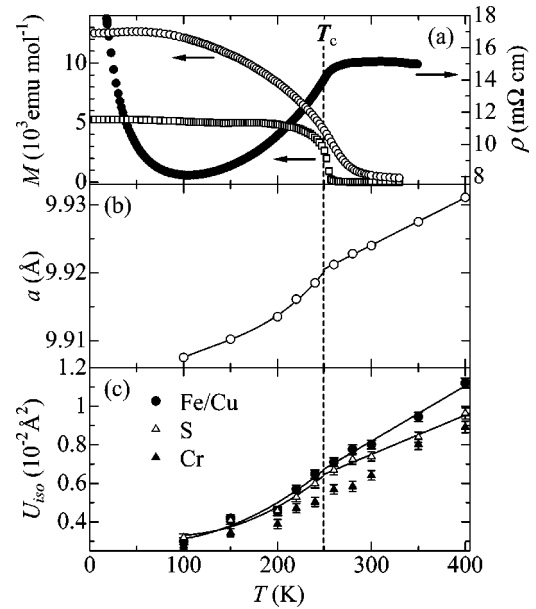


FIG. 1. The temperature dependence of (a) magnetization [ $H=0.01$  T (open squares) and 2 T (open circles)] and electric resistivity ( $H=0$  T), (b) the cubic lattice parameter, and (c) the isotropic Debye-Waller factor for each atomic site, in  $\text{Fe}_{0.8}\text{Cu}_{0.2}\text{Cr}_2\text{S}_4$ . In (b), the error bars are smaller than the symbols. The solid lines are guides to the eye.

the isotropic Debye-Waller factor  $U_{iso}$  for each site. It is clearly observed that  $U_{iso}$  of S [ $U_{iso}(\text{S})$ ] shows a behavior similar to oxygen in the perovskites, closely resembling the  $T$  dependence of  $a$ . More specifically,  $U_{iso}(\text{S})$  is large and weakly  $T$  dependent for  $T > T_c$ , suggesting the presence of a disordered displacement field. At  $T_c$ ,  $U_{iso}(\text{S})$  suddenly drops and acquires a pronounced  $T$  dependence, which is consistent with a crossover into a typical phonon regime.<sup>5</sup> A much weaker but noticeable change in  $U_{iso}$  at  $T_c$  is observed for the Fe/Cu site, suggesting that the distortion is coupled to the A site. In contrast,  $U_{iso}$  for Cr shows a much smaller discontinuity across  $T_c$ , indicating that the influence of distortion is greatly reduced for the Cr atoms.

The close resemblance in the changes of lattice parameter and  $U_{iso}$  at  $T_c$  for  $\text{Fe}_{0.8}\text{Cu}_{0.2}\text{Cr}_2\text{S}_4$  and the CMR perovskites suggests that similar electron-phonon coupling mechanism is operative, and it seems reasonable to expect the JT distortion of the  $\text{Fe}^{2+}\text{S}_4$  tetrahedra to play a similar role to that of the  $\text{Mn}^{3+}\text{O}_6$  octahedra. Indeed, it is known that an  $\text{Fe}^{2+}$  ion in the tetrahedral environment of the spinel A site exhibits a significant JT effect, which can result in cooperative JT transition<sup>22</sup> or large magnetostriction arising from strong spin-lattice coupling.<sup>23</sup> On the other hand,  $T_{JT} \sim 10$  K in  $\text{FeCr}_2\text{S}_4$  is much smaller than  $T_{JT} \sim 750$  K in the parent perovskite  $\text{LaMnO}_3$ , and it is not immediately obvious that the energy scale associated with the local JT distortion is large enough to affect the lattice properties at  $T_c > 170$  K in  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ . Nevertheless, the estimate<sup>13</sup> based on Mössbauer data shows that the local JT distortion has the energy scale of at least room temperature, and the presence of dynamic JT distortion above  $T_{JT}$  has been discussed in the literature.<sup>12</sup> Moreover, the much lower  $T_{JT}$  in  $\text{FeCr}_2\text{S}_4$  com-

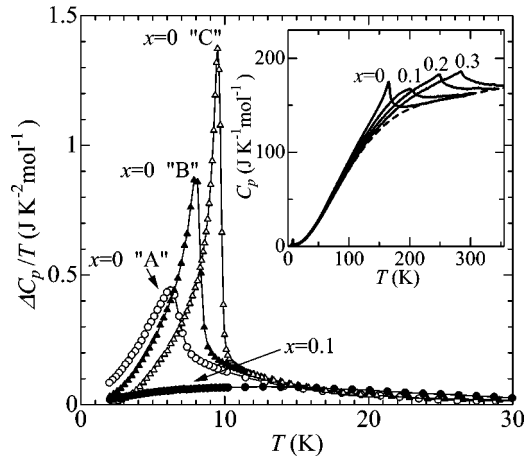


FIG. 2. The low-temperature heat capacity  $C_p$  for  $x=0.1$  and the three samples of  $x=0$ . The lattice and spin-wave contributions were subtracted from the data. The inset shows  $C_p$  of  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  ( $0 \leq x \leq 0.3$ ). The data from sample B are plotted for  $x=0$ , but samples A and C show almost identical behavior except for  $T < 20$  K. The dashed line denotes the baseline used to estimate entropy.

pared to  $\text{LaMnO}_3$  can be attributed partly to the difference in connectivity: In perovskites, each oxygen is shared by two Mn ions, and distortions on adjacent sites are directly coupled. On the other hand, the tetrahedral S ions in spinels are not connected directly, resulting in much weaker cooperative effects.

The presence of dynamic JT distortion in  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  may also explain various aspects of the transport properties. A detailed study of resistivity and thermopower<sup>24</sup> on Zn-doped  $\text{FeCr}_2\text{S}_4$  showed strong evidence of polaron conductivity for  $T > T_c$ , which would be consistent with a hopping conductivity involving JT-active  $\text{Fe}^{2+}$ . Also, the size of magnetoresistance, which decreases gradually with increasing  $x$  (Ref. 18) despite the nonmonotonic change in  $\rho$ , could be directly related to the concentration of JT-active  $\text{Fe}^{2+}$ .

To better understand the nature of the transition, as well as its evolution with  $x$ , we show  $C_p$  up to 350 K for  $0 \leq x \leq 0.3$  in the inset of Fig. 2. For each  $x$ , we observe a clear anomaly in  $C_p$  that marks the onset of second-order ferrimagnetic transition. The sharpest peak is observed for  $x=0$ , and the peak broadens with increasing  $x$ . The gradual change in the shape of magnetic  $C_p$  with  $x$  is in sharp contrast to the perovskites, where  $C_p$  varies significantly with  $x$  and even the order of transition changes with the doping level.<sup>25</sup> In order to obtain the entropy of the transition  $\Delta S$ , we have estimated the lattice contribution as shown in the figure as a dashed line. The obtained value of  $\Delta S$  decreased continuously from 19 to 12  $\text{J K}^{-1} \text{mol}^{-1}$  between  $x=0$  and 0.3. These values are all smaller than the expected full spin values (e.g., 36  $\text{J K}^{-1} \text{mol}^{-1}$  for  $x=0$ ), presumably due to the presence of short-range order at higher  $T$ .<sup>26</sup> However, the decrease in  $\Delta S$  with increasing  $x$  is consistent with the change in the average spin quantum number, suggesting that  $\Delta S$  is mostly accounted for by the spin degree of freedom. These results, together with the monotonous increase with  $x$  in  $T_c$  and the saturation moment, are consistent with the as-

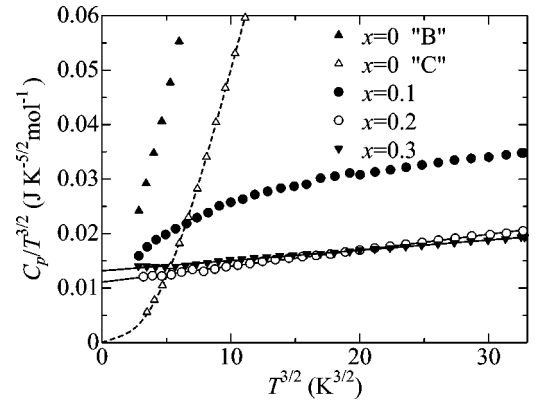


FIG. 3. The low-temperature heat capacity of  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  ( $0 \leq x \leq 0.3$ ) plotted as  $C_p/T^{3/2}$  vs  $T^{3/2}$ . The solid lines are the linear fits. The dashed line is a fit to the spin-gap form as described in the text.

sumption that the magnetic exchange is mediated by bound electrons (direct exchange and superexchange), and that conduction electrons play a minor role in the magnetic exchange. Therefore, CMR in  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  arises from the strong  $T$  dependence of  $\rho$  due to magnetic ordering, which in turn is mediated by localized electrons. This magnetotransport coupling seems to be independent of the absolute value of conductivity, which is strongly enhanced by the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  heterovalency.<sup>15,18</sup> These relationships between magnetism and transport are in striking contrast to the doped perovskites, where transfer of charge carriers directly mediate the ferromagnetic exchange. Thus, although mixed-valence conductivity and strong lattice effects are important aspects of transport in both  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  and the perovskites, these are essential for CMR only in the perovskites; this is most evident from the observation of CMR even for  $x=0$  and 0.5 in  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ .<sup>11</sup>

The main panel of Fig. 2 shows the low- $T$   $C_p$  for  $x=0.1$ , and the three samples (referred to as A, B, and C) of  $x=0$  with the slightly different Fe/Cr ratio as described above. The lattice and spin-wave contributions have been subtracted.<sup>27</sup> For  $x=0.1$ , a broad feature that extends to high  $T$  is observed.<sup>28</sup> For sample C of  $x=0$ , there is a sharp lambda-type anomaly whose peak locates  $T_{\text{JT}}=9.6$  K. For samples B and A, the peak becomes progressively smaller in magnitude and is shifted down in  $T$ . These results are consistent with the earlier study<sup>29</sup> that showed that a slightly excess Cr over Fe in the starting composition is needed to prevent the Fe incorporation into the Cr site (Cr ions do not substitute for the A site). The strong sensitivity of orbital ordering to defects is in contrast to the magnetic ordering, in which  $T_c$  changed by less than 2% among the three samples of  $x=0$ . Since sample C contains a small amount of  $\text{Cr}_2\text{S}_3$  and  $T_{\text{JT}}=9.6$  K is higher than the previously reported values,<sup>29</sup> it is expected to be fully stoichiometric. Also, even for sample C, which shows the largest entropy associated with the transition, the obtained entropy of 3.8  $\text{J K}^{-1} \text{mol}^{-1}$  is less than 70% of the expected value of  $R \ln 2$ . This result is consistent with the presence of short-range order at higher  $T$ , which in turn underscores the significance of dynamic JT distortions.

The evolution of ground-state properties with  $x$  can be tracked in Fig. 3, where the low- $T$   $C_p$  is plotted as  $C_p/T^{3/2}$  vs  $T^{3/2}$ . For  $x=0.3$  and  $0.2$ , the data show a linear behavior, indicating that  $C_p$  obeys the relation  $C_p = \delta T^{3/2} + \beta T^3$  with the intercept  $\delta$  due to ferrimagnetic spin waves and the slope  $\beta$  due to lattice. The insulating ground state of these systems is confirmed by the absence of a linear term. The larger value of  $\delta$  for  $x=0.3$  ( $13.2 \text{ mJ K}^{-5/2} \text{ mol}^{-1}$ ) compared to  $0.2$  ( $11.1 \text{ mJ K}^{-5/2} \text{ mol}^{-1}$ ) is consistent with the higher saturation moment in the former. The larger value of  $\beta$  for  $x=0.2$  compared to  $0.3$  translates to lower Debye temperature  $\Theta_D$  in the former (360 and 420 K, respectively). This is opposite to the expectation based on the molecular weight, and may be attributed to the larger amount of JT-active ion in the former, as has been discussed for the perovskites.<sup>30</sup> Qualitatively different behavior is observed for  $x=0$  and  $0.1$ , which show orbital ordering. For these compositions,  $C_p$  extrapolates to 0 for  $T \rightarrow 0$  K, indicating that the orbital ordering results in the opening of a spin gap. A fit by the expression  $C_p$

$= AT^{3/2} \exp(-\Delta/T) + \beta T^3$  for sample C of  $x=0$  (the dashed line in Fig. 3) yields the gap energy of  $\Delta = 13(1) \text{ K} = 1.1(1) \text{ meV}$  and  $\beta$  corresponding to  $\Theta_D = 260 \text{ K}$ .<sup>31</sup> It is interesting to note that an energy gap of  $1.7 \text{ meV}$  in low- $T$   $C_p$  was recently observed in  $\text{LaMnO}_3$ .<sup>32</sup>

In conclusion, our study shows that electronic and magnetic properties in spinel  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$  are critically linked to the lattice through the orbital degree of freedom, in a manner that is strikingly similar to the perovskite manganites. Thus, similarly rich physics can be expected to be fully elucidated in the heterovalent chalcogenide spinels, where, unlike the perovskites, both the  $A$  and  $B$  sites can participate in transport and magnetism.

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- <sup>20</sup> Refinement ( $3^\circ \leq 2\theta \leq 40^\circ$ ) was carried out in space group  $Fd\bar{3}m$  for all  $T$ , and the atomic position of the S site was refined simultaneously. No significant deviation from full occupancy was observed for each site, and subsequent refinement was carried out with the site occupancies kept at fixed values consistent with the nominal stoichiometry. For the 300-K refinement, the final agreement indices were  $R_{wp} = 7.33\%$ ,  $R_I = 3.31\%$ ,  $R_F = 1.95\%$ , and  $S = 1.59$ . Similar indices were obtained for other  $T$ .
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- <sup>27</sup> The baseline was obtained by subtracting the spin-wave contribution from the  $x=0.2$  data and scaling  $T$  by 0.9. This baseline coincides with  $C_p$  between 30 and 70 K for  $x=0$  and between 45 and 70 K for  $x=0.1$ .
- <sup>28</sup> After the original submission of this paper, Fichtl *et al.* [R. Fichtl *et al.*, *Phys. Rev. Lett.* **94**, 027601 (2005)] reported “orbital glass” behavior in single crystalline  $\text{FeCr}_2\text{S}_4$ , which shows  $C_p$  similar to our data on  $x=0.1$ . The intriguing behavior may be due to nonstoichiometry associated with the Cl-vapor growth method.
- <sup>29</sup> F. K. Lotgering, A. M. van Diepen, and J. F. Olijhoek, *Solid State Commun.* **17**, 1149 (1975).
- <sup>30</sup> T. Okuda *et al.*, *Phys. Rev. Lett.* **81**, 3203 (1998).
- <sup>31</sup> The uncertainty in the  $\Delta$  value is from various fits with the upper  $T$  limit varied between 4–7 K. No systematic range dependence was observed. Tsurkan *et al.* [cond-mat/0407026 (unpublished)], deduced an energy gap of  $11.4 \text{ K}$  from their low- $T$   $C_p$  data using a different function.
- <sup>32</sup> V. Fritsch *et al.*, *Phys. Rev. B* **65**, 212405 (2002).