

## X-ray-induced disordering of the dimerization pattern and apparent low-temperature enhancement of lattice symmetry in spinel $\text{CuIr}_2\text{S}_4$

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At low temperatures, spinel  $\text{CuIr}_2\text{S}_4$  is a charge-ordered spin-dimerized insulator with triclinic lattice symmetry. We find that x rays induce a structural transition in which the local triclinic structure is preserved, but the average lattice symmetry becomes tetragonal. These structural changes are accompanied by a thousandfold reduction in the electrical resistivity. The transition is persistent, but the original state can be restored by thermal annealing. We argue that x-ray irradiation disorders the lattice dimerization pattern, producing a state in which the orientation of the dimers is preserved, but the translational long-range order is destroyed.

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Spinel compounds  $AB_2X_4$  ( $X$  is O, S, Se, or Cl) have attracted much attention over the last decade because they exhibit a large variety of interesting ground states, including superconductivity, cooperative antiferromagnetism, heavy fermion, and charge-ordered and spin-dimerized states.<sup>1,2</sup> The panoply of different properties exhibited by spinels results from the interplay of Coulomb interactions, effects of frustrated magnetism, and electron-lattice interaction. The corner sharing tetrahedral network of  $B$  sites in the spinel structure can accommodate a large number of different charge-ordering patterns. In fact, some of the most complex charge-ordering patterns reported to date are found in spinel compounds.<sup>3,4</sup> The same tetrahedral network gives rise to geometric magnetic frustration when the ions occupying the  $B$  site are magnetic. The electronic and magnetic states realized in such a complex environment are often multidegenerate and strongly fluctuating. Because of these complexities, a number of properties of the spinels remain poorly understood. Spinel, therefore, are important subjects of research in the physics of strongly correlated materials. In addition, some of these compounds, such as the lithium manganese spinels used in battery cathodes and the ferrites used in microwave applications, are of substantial technological importance.

Chalcogenide spinel  $\text{CuIr}_2\text{S}_4$  has attracted attention because this compound undergoes a sharp metal-insulator transition at  $T_{MI} \approx 230$  K.<sup>5</sup> The low-temperature insulating state is nonmagnetic. Nuclear magnetic resonance and photoemission experiments have shown that the Cu ion is monovalent in the insulating phase, and therefore the nominal valence of the iridium atoms is 3.5.<sup>6</sup> It was proposed that charge ordering of  $\text{Ir}^{3+}$  ( $S=0$ ) and  $\text{Ir}^{4+}$  ( $S=1/2$ ) ions is the origin of the metal-insulator transition in  $\text{CuIr}_2\text{S}_4$ ,<sup>5</sup> and that some kind of spin dimerization is responsible for the nonmagnetic nature of the insulating phase.

Recent experimental determination of the low-temperature structure<sup>3</sup> has provided very strong evidence that this scenario is correct. Specifically, these experiments have

shown that the Ir sublattice consists of two types of Ir capped hexagonal rings, which were described as  $\text{Ir}_8^{3+}$  and  $\text{Ir}_8^{4+}$  octamers. The  $S=1/2$   $\text{Ir}^{4+}$  ions were found to form structural dimers, which were also identified as spin dimers. The magnitude of the lattice distortion due to this dimerization is truly remarkable: the Ir-Ir distance in the dimers is  $\sim 3.0$  Å, while all the other Ir-Ir nearest-neighbor distances are between 3.43 and 3.66 Å. Inset in Fig. 1 illustrates the low-temperature charge ordering and spin-dimerization pattern reported in Ref. 3. The low-temperature state possesses triclinic symmetry.<sup>7,3</sup> However, for simplicity, we describe the structure of  $\text{CuIr}_2\text{S}_4$  using the conventional cubic spinel unit cell, which is not the true unit cell at low temperatures.

In this work, we report high-resolution x-ray powder diffraction and simultaneous electrical resistance measurements on  $\text{CuIr}_2\text{S}_4$ . We find that at low temperatures, x rays induce

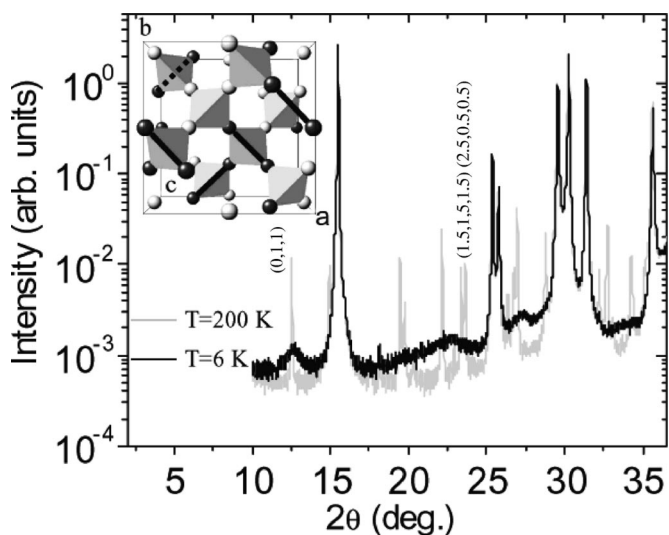


FIG. 1. X-ray powder scans at  $T=200$  K and  $T=6$  K,  $\lambda = 1.5406$  Å. The inset shows the charge-ordering pattern in the triclinic state.  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  ions are shown in white and black, respectively. Black bonds indicate dimerized  $\text{Ir}^{4+}$  ions.

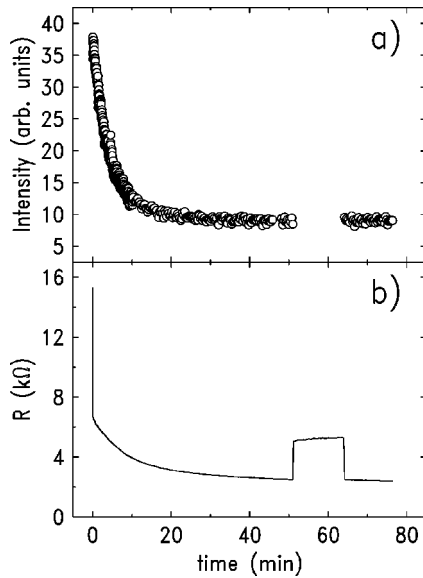


FIG. 2. X-ray exposure dependence of (a) the intensity of the (2,2,1) superlattice peak and (b) electrical resistance at  $T=10$  K. X rays were switched off between  $t=51$  min and  $t=64$  min.

a triclinic-to-tetragonal structural transition in which the electrical resistivity is reduced by a factor of  $10^3$ . The transition is persistent, but the original state can be restored by heating above  $T\sim 100$  K and subsequent cooling. To our knowledge, the only other example of such a dramatic reversible x-ray-induced structural change is found in perovskite manganites, in which x rays convert a charge-ordered insulator to ferromagnetic metal.<sup>8</sup> In our samples, all the Bragg peaks in the x-ray converted state can be accounted for using the tetragonal  $I4_1/amd$  space group. However, analysis of the diffuse x-ray scattering in the tetragonal state shows that the triclinic structure is preserved locally. Therefore, x-ray irradiation changes only the average (or global) symmetry. We argue that this apparent change in the lattice symmetry is caused by x-ray-induced disordering of the lattice dimerization pattern, in which the orientation of the  $\text{Ir}^{4+}$  dimers is preserved. Tetragonal  $\text{CuIr}_2\text{S}_4$  provides, therefore, an interesting example of a state possessing rotational, but not translational, long range dimer order.

Polycrystalline samples of  $\text{CuIr}_2\text{S}_4$  were prepared by a solid reaction method. The mixtures of Cu, Ir, and S powders were heated in an evacuated quartz tube at  $800\text{--}900^\circ\text{C}$  for eight days. The samples were then ground, pressed into a pellet, and sintered in vacuum at  $900^\circ\text{C}$  for another three days. X-ray powder-diffraction measurements were carried out at beam lines X20C and X25 at the National Synchrotron Light Source. An x-ray beam was focused by a mirror, monochromatized by a double-crystal Si (111) monochromator, and analyzed with Ge (111) crystal. The wavelengths used were  $\lambda=1.513$  and  $1.5406$  Å, the beam size was  $\sim 1$  mm<sup>2</sup>, and the typical intensity was  $10^{11}$  photons/sec. The sample was mounted in a closed-cycle refrigerator ( $T=6\text{--}300$  K). The powder patterns were measured using the  $\theta/2\theta$  step scanning mode. For electrical resistivity measurements, four gold contacts were evaporated on the surface of

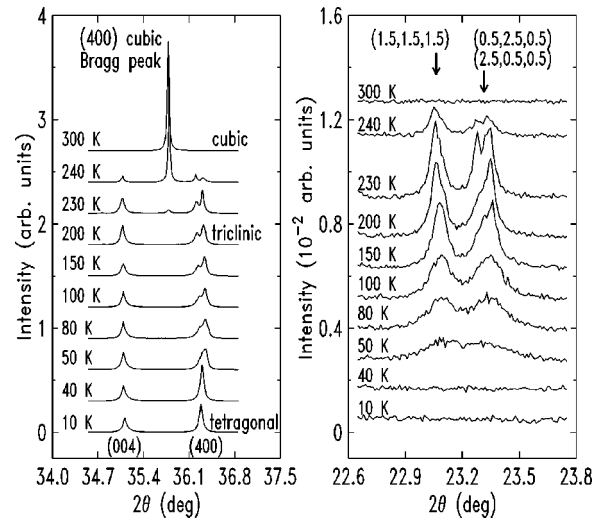


FIG. 3. X-ray scans in the vicinity of the (400) cubic Bragg peak, and the (1.5,1.5,1.5), (0.5,2.5,0.5), and (2.5,0.5,0.5) superlattice peaks at various temperatures, taken on heating. X-ray wavelength  $\lambda=1.513$  Å.

the polycrystalline sample. The x-ray beam was hitting the sample in between the contacts, and x-ray diffraction and electrical resistance measurements were done simultaneously. Neutron-powder-diffraction data were collected using the HRPD high-resolution powder diffractometer at the ISIS facility.

Figure 1 shows partial x-ray scans taken at  $T=6$  K and  $T=200$  K. Note that the x-ray intensity is shown on a logarithmic scale. The  $T=6$  K scan was taken after several hours of initial exposure to x rays. All the Bragg peaks at  $T=6$  K can be indexed assuming the tetragonal symmetry with the space group  $I4_1/amd$  and lattice constants  $a=6.8766$  Å and  $c=10.039$  Å, with the  $a$  and  $b$  axes pointing along the (110) and (1-10) directions in the cubic spinel unit cell. At  $T=200$  K, the structure is triclinic. For  $T>T_{MI}\approx 230$  K,  $\text{CuIr}_2\text{S}_4$  exhibits an undistorted cubic spinel structure. In this work, all the Bragg peaks are indexed using the cubic spinel unit cell with lattice constant  $a\sim 9.8$  Å. Note that this indexing scheme is only approximate for  $T<T_{MI}$ . In the triclinic state, a number of peaks that are not present in the cubic and the tetragonal phase appear (see Fig. 1). We refer to these peaks as superlattice peaks.

According to our neutron-diffraction measurements taken after the sample was equilibrated for 12 h at  $T=4$  K, the low-temperature state of  $\text{CuIr}_2\text{S}_4$  is triclinic. The tetragonal state is induced by x rays. Figure 2(a) shows that a 30 min x-ray exposure completely destroys the superlattice peaks. At the same time, the resistance of the sample is significantly reduced, see Fig 2(b). When the x rays are switched off, the resistance increases abruptly (most likely due to beam heating effects), and then keeps increasing with a time constant  $\tau>5$  h. It is possible, therefore, that the x-ray induced state is metastable. Even after a 10 h wait, however, the resistance does not reach a third of its original value, and no detectable superlattice peaks are observed after 24 h. In our experimental geometry, x rays penetrated only  $\sim 2$  μm into the sample,

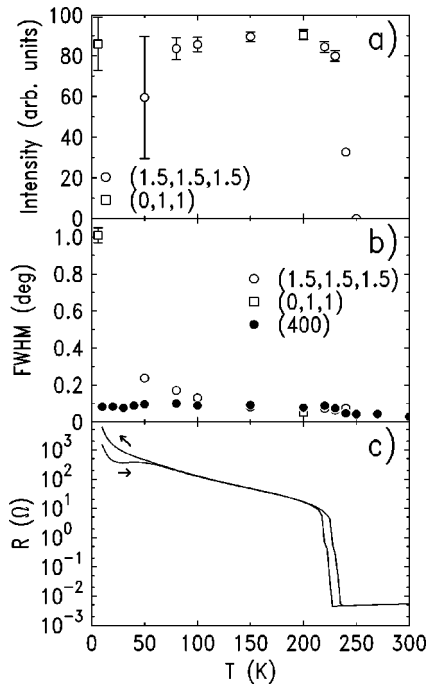


FIG. 4. Temperature dependence of (a) the integrated intensity of the  $(1.5, 1.5, 1.5)$  and  $(0, 1, 1)$  superlattice peaks, (b) full width at half maximum of the same superlattice peaks and of the  $(400)$  Bragg peak, and (c) electrical resistance. The data were taken on heating from the x ray converted state. Electrical resistance taken on cooling with no x-rays present is also shown. The  $(0, 1, 1)$  peak intensity in (a) was normalized to match the  $(1.5, 1.5, 1.5)$  intensity at  $T=200$  K.

and therefore only a small surface layer of the sample was undergoing the x-ray-induced transition. Assuming that the thickness of this layer is equal to the x-ray penetration depth, we estimate that the resistivity of the tetragonal state is approximately  $2 \Omega \text{ cm}$ . This is at least three orders of magnitude smaller than the resistivity of the triclinic phase in polycrystalline  $\text{CuIr}_2\text{S}_4$ .<sup>5,9</sup>

The triclinic state recovers when the sample is heated above 100 K, even in the presence of x rays. In Figure 3, scans in the vicinity of the  $(4, 0, 0)$  main Bragg peak and the  $(1.5, 1.5, 1.5)$  superlattice peak taken on heating at different temperatures are shown. The triclinic state manifests itself by splitting of the tetragonal peaks and by the appearance of the superlattice peaks. The superlattice peaks are very broad at low temperatures. A careful examination of the x-ray scan at  $T=6$  K in Fig. 1 shows that enhanced diffuse scattering exhibiting broad features with maximums near the superlattice peak positions is present in the tetragonal state. Such a broad feature can be seen, for example, at the  $(0, 1, 1)$  superlattice peak position at  $2\theta=12.7^\circ$ . Broadening of the diffraction peaks is associated with finite correlation length of the ordered state. Therefore, short-range-ordered triclinic regions, and the associated  $\text{Ir}^{4+}$  dimers, are present even in the x-ray converted state. Unlike the superlattice peaks, the main Bragg peaks remain narrow in the entire temperature range.

Figure 4 shows the integrated intensity of the  $(0, 1, 1)$  and  $(1.5, 1.5, 1.5)$  superlattice peaks, and the superlattice peak

width taken at different temperatures on heating from the x-ray converted state. These data were obtained from the scans shown in Figs. 1 and 3 using Lorentzian fits. The integrated intensity is the same in both the triclinic and the tetragonal states, within experimental errors. Therefore, on the local level, the structure is triclinic everywhere in the x-ray converted state. The correlation length of the triclinic lattice distortion, estimated from the width of the  $(0, 1, 1)$  peak, is  $\xi_{ir} \sim 30 \text{ \AA}$  at  $T=6$  K.

Dimerization of  $\text{Ir}^{4+}$  is the dominant source of the triclinic lattice distortion, and therefore, the long-range correlation between the dimers is lost in the tetragonal state. We propose the following scenario of the x-ray-induced transition. X rays remove localized electrons from the Ir atoms, thereby instantaneously destroying local charge ordering and lattice dimerization pattern. The electrons quickly relax, and the charge ordering is restored. However,  $\text{Ir}^{4+}$  dimers do not necessarily form in the original places. This is, in fact, not unexpected, if one takes into account that slowly propagating elastic interactions play a dominant role in the formation of the dimerization pattern in  $\text{CuIr}_2\text{S}_4$ . The Coulomb interaction is less important in this compound, as indicated by the breakdown of the Anderson's condition which requires that two  $\text{Ir}^{3+}$  and two  $\text{Ir}^{4+}$  ions are present in every Ir tetrahedron (see inset in Fig. 1). It is interesting to note that the correlation length  $\xi_{ir}$  is large enough to accommodate several Ir octamers. This indicates that the  $\text{Ir}^{4+}$  dimers still tend to form the octamer units in the tetragonal state, and therefore these octamers are quite robust.

Rietveld refinement of the powder data in the x-ray converted tetragonal state can only provide the average structure. In fact, in the  $I4_1/amd$  group, all the Ir atoms are equivalent, and no direct information about the Ir charge order can be obtained in a conventional refinement. Experiments on single crystals will eventually be required to determine the local structure of the tetragonal state, and x-ray photon spectroscopy or near-edge x-ray-absorption fine structure measurements will be needed to study the valence state of the Ir atoms in the irradiated samples. We have, however, attempted the Rietveld refinement of the powder data at  $T=6$  K putting  $\text{Ir}^{3+}$  ions in the  $8d$  site with occupation 0.5, and  $\text{Ir}^{4+}$  ions in the  $16h$  site with occupation 0.25. The refinement produced two  $\text{Ir}^{4+}$  ions in each  $16h$  site displaced along the  $[110]$  cubic direction with respect to each other. Since in the triclinic state the  $\text{Ir}^{4+}$  dimers form along the same direction,<sup>10</sup> this result is consistent with the assumption that uncorrelated dimers are present in the sample. It also indicates that the dimers in the x-ray converted state form along the same direction as in the triclinic phase. Moreover, the intradimer distance obtained in our refinement,  $3.09 \text{ \AA}$ , is close to the actual value found in the triclinic state. While the overall quality of the fit is only average ( $R_{wp}=0.100$ ), the fit is consistent with the disordering scenario proposed above. Further details of the Rietveld refinement will be given elsewhere.<sup>9</sup>

In addition to the results of the Rietveld refinement, the increased value of the  $c$  lattice constant in the tetragonal state provides an evidence that the  $\text{Ir}^{4+}$  dimers remain contained in the  $ab$  plane and, therefore, do not change their orienta-

tion. The long-range translational order of the dimers, on the other hand, is clearly destroyed in the tetragonal state. An interesting question, which requires further investigation, is whether the tetragonal state in  $\text{CuIr}_2\text{S}_4$  could be considered a thermodynamic phase, with some properties, possibly, resembling those of liquid-crystal phases. To answer this question, the equilibrium thermal properties of the tetragonal state need to be investigated. As was mentioned above, the x-ray-induced state is in all likelihood metastable. However, it might be possible that the equilibrium tetragonal state can be induced by other sources of disorder. In particular, static disorder from chemical substitution appears to be promising. To test this proposal, experiments with  $\text{Cu}(\text{Ir,Cr})_2\text{S}_4$  samples are currently under way.

The reduced electrical resistivity in the x-ray converted state most likely results from the imperfections in the charge order. Charge-disordered conducting regions might form, for instance, at the boundaries between the ordered triclinic domains. Consistent with this assumption, the resistivity characteristic to the triclinic state is recovered on heating, as these imperfections disappear and the long-range ordered triclinic state is restored, see Fig. 4(c).

Finally, we note that in a recent paper, Sun *et al.* reported an electron diffraction experiment suggesting a structural transition in  $\text{CuIr}_2\text{S}_4$  at  $T < \sim 50$  K.<sup>11</sup> We speculate that this transition is of the same nature as the x-ray-induced transition described above, and that it is induced by an electron beam.

In summary, we find that x rays induce an apparent triclinic-to-tetragonal transition in  $\text{CuIr}_2\text{S}_4$  at low temperatures. In addition to the drastic structural changes, x-ray irradiation reduces the electrical resistivity by at least three orders of magnitude. The triclinic state can be recovered by thermal annealing. We argue that the transition results from the x-ray-induced disorder in the  $\text{Ir}^{4+}$  dimerization pattern, in which the orientation of the dimers is preserved, but the translational long-range order is destroyed.

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