Incommensurate Structural Correlations in the Disordered Spin-Dimer State Induced by X-Ray and Electron Irradiation in $CuIr_2S_4$

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Irradiation with ~10 keV x rays or medium-energy electrons destroys long-range order of Ir spin dimers in $CuIr_2S_4$ while preserving the dimers locally. We find that as the order is destroyed, a new type of incommensurate structural correlations appears. This represents an intriguing example of order from disorder phenomenon, in which a previously unknown incommensurate order appears in the radiation-induced disordered state. These results suggest that two competing instabilities, one of which can be suppressed by radiation, are present in the system. Otherwise unrealized structural or electronic states can, therefore, be revealed in correlated systems by x-ray or electron irradiation.

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Transition-metal spinel compounds AB_2X_4 (X is O, S, or Se) have attracted much attention over the last decade because they exhibit a large variety of exotic magnetic and electronic ground states [1]. The intriguing properties of spinels can usually be attributed to the geometrically frustrated magnetic or electronic interactions characteristic to the corner sharing tetrahedral network of B sites, known as the pyrochlore lattice. Even when only magnetic interactions are present, geometric frustration gives rise to novel quantum states, such as spin ice and spin liquid, and to unusual collective excitations [2,3]. When the charge degree of freedom is added to the system, an intriguing possibility of charge order (CO) and orbital order (OO) on a frustrated lattice is realized. The CO and OO patterns observed in this case are the subject of intense current interest. In fact, some of the most complex CO patterns known thus far have been found in spinels [4,5]. Many of the CO structures in spinels, including that of the prototype CO compound Fe_3O_4, remain to be determined [1].

Spinels in which both the charge and magnetic degrees of freedom are present provide unique possibilities for observation of novel ground states. The pyrochlore lattice is known to support a large number of ordered and disordered configurations with similar energies, and complex phase diagrams and unusual transitions are therefore expected in this case, especially if competing interactions are present [1]. A recent success story in the field is the experimental determination and theoretical description of the complex CO and spin dimerization pattern in the mixed valence spinel $CuIr_2S_4$ [4]. The CO state is unstable against x-ray (~ 10 keV) irradiation, which destroys the long-range charge order while preserving it locally [6]. In this work, we report that as the long-range order is destroyed by an x-ray or an electron beam, previously unknown incommensurate structural correlations appear in the system. This represents an intriguing example of order from disorder phenomenon, in which a new incommensurate order appears in the radiation-induced disordered state. The simplest explanation of these results involves a competing instability, such as a charge density wave (CDW) for instance, that is revealed as the long-range CO is suppressed. X-ray or electron irradiation can, therefore, be used as a tool that can reveal otherwise unrealized instabilities in systems with competing ground states.

The nominal valence of the Ir atoms in $CuIr_2S_4$ is 3.5 [7]. For $T < T_{CO} \approx 230$ K, $CuIr_2S_4$ exhibits long-range order of Ir^{3+} ($S = 0$) and Ir^{4+} ($S = 1/2$) ions [4,8]. Ir chains with the repeating pattern $Ir^{3+}Ir^{4+}Ir^{4+}Ir^{3+}$ form in the ab plane, and the $S = 1/2$ Ir^{4+} ions form nonmagnetic dimers. The Ir-Ir distance in the dimers (~3.0 Å) is much smaller than the distance between the other Ir atoms (~3.5 Å) [4]. It was proposed that because of the pseudotetragonal distortion of the crystal lattice, the available carriers (holes) occupy the d_{xy} t_{2g} Ir orbitals which lie in the ab plane [9,10]. This makes the Ir chains described above effectively one-dimensional (1D). The upper t_{2g} orbitals therefore form a 1/4-occupied 1D band, and Peierls tetramerization of the Ir chains explains the observed structure [9]. A model describing spin dimerization in spinels using a local spin-orbital Hamiltonian has also been proposed [11].

In this work, we report x-ray diffraction (XRD) and electron diffraction (ED) studies of the radiation-induced state in $CuIr_2S_4$. Polycrystalline samples were prepared as described in Ref. [6]. To prepare single crystals, they were mixed with Bi powder at 1:100 molar ratio, and then cooled down in evacuated quartz ampoules from 1050 °C at 3 °C/h rate. X-ray diffraction measurements were carried out at beam line X22C at the National Synchrotron Light Source. An x-ray beam of energy 8.8 keV, ~1 mm^2 in cross section, and the typical intensity of 10^{11} photon/s

was used. The ED data were collected using a JEOL-2000FX transmission electron microscope operating at 200 kV with typical electron beam intensity of 5 mA/cm^2. Specimens for the ED studies were prepared by mechanical polishing followed by Ar-ion milling. The x-ray-induced disordered state of $CuIr_2S_4$ is tetragonal, space group $I4_1/amd$, with lattice constants $a_t = 6.8766$ Å and $c_t = 10.039$ Å at $T = 6$ K [6]. The a_t axes run along the [110] and [1–10] cubic spinel directions, and $a_t \approx a/\sqrt{2}$, $c_t \approx a$, where a is the lattice constant of the high-temperature cubic unit cell. The long-range CO state exhibits an additional small triclinic lattice distortion [4]. In this Letter, all positions (HKL) in the reciprocal space are indexed using the pseudocubic axes with the L direction chosen to coincide with the tetragonal axis c_t.

Irradiation with an x-ray or an electron beam destroys the long-range charge order in $CuIr_2S_4$ for $T_{irr} < 50$ K [6]. (We use T_{irr} for the temperature at which the sample was irradiated to induce structural conversion, and T for the temperature at which the subsequent measurements were made.) The average structure determined in x-ray powder diffraction experiments does not show any Ir dimerization. Advanced analysis of the powder x-ray data strongly suggests, however, that most of the Ir^{4+} dimers remain in the same Ir chains in the x-ray-induced state [6]. No long-range correlations between the dimers were found, and it was proposed that the disordered dimers are only weakly correlated in the Ir chains [6].

Our measurements reveal that the radiation-induced state possesses a much more elaborate structure. Figure 1 shows electron diffraction patterns for $T = T_{irr} = 93$ K and $T = T_{irr} = 19$ K with the incident beam parallel to the [1–10] cubic axis. Electrons and x rays induce the tetragonal state only for $T_{irr} < 50$ K, and the $T = 93$ K pattern shows the long-range ordered state. Two types of Bragg peaks that are not present in the electron-induced state are observed at $T = 93$ K. They correspond to the (HHL), $H + L$ odd, and $(0.5, 0.5, 0.5)$ propagation vectors. The peaks of the first type are forbidden in the tetragonal $I4_1/amd$ structure, and we refer to them as the F peaks. The peaks of the second type are called the superlattice, or S peaks. Both the F and S peaks result from the ordered pattern of the Ir^{4+} dimers in the Ir chains [4]. Electron irradiation has very different effects on the F and S peaks. The S peaks disappear without a trace in the irradiated state at $T = 19$ K. Sharp Bragg peaks also disappear in the F positions. However, strong diffuse scattering is present in the vicinity of the F positions in the electron-converted state, as Fig. 1(b) clearly shows. In itself, this observation is not entirely surprising. Indeed, the $(0.5, 0.5, 0.5)$ propagation vector reflects longer-range correlations between the dimers in the Ir chains, and between the chains themselves. Scattering in the F positions, on the other hand, signals the breakdown of the body-centering operator within the tetragonal unit cell. This happens in any structure in which one half of the Ir atoms is dimerized, as in $CuIr_2S_4$. Thus, if the Ir dimers are correlated only on the length scale of the tetragonal unit cell, diffuse scattering is expected in the F, but not in the S, positions. We note that short-range interdimer correlations are indeed expected because of the large structural distortions associated with the Ir dimers.

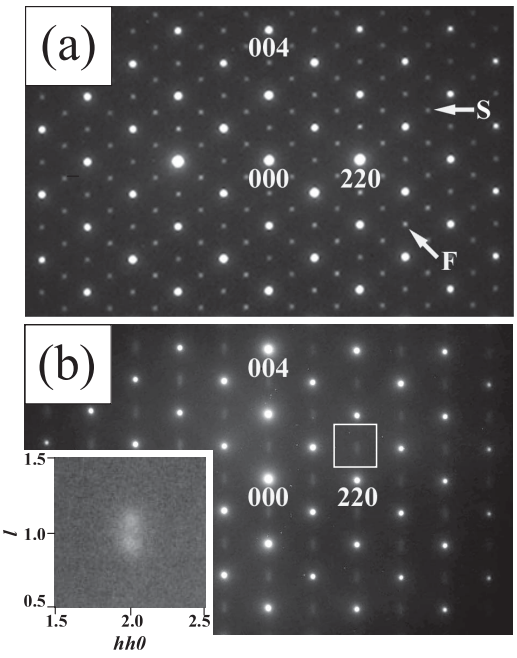

FIG. 1. Electron diffraction patterns for (a) $T = T_{irr} = 93$ K and (b) $T = T_{irr} = 19$ K. The incident beam is parallel to the [1–10] cubic axis. The inset in (b) shows the enlargement of the diffraction pattern in the vicinity of the $(2, 2, 1)$ position at $T = 19$ K.

Inspection of the diffuse scattering in the F position reveals, however, a surprising result. As the inset of Fig. 1(b) shows, the diffuse scattering is comprised of two broad peaks in incommensurate (IC) positions. Additional diffraction measurements show that this scattering feature is of a dumbbell shape, i.e., consists of two overlapping nearly spherical ellipsoids in the three-dimensional reciprocal space. Therefore, the lattice distortion ascribed to the local Ir dimer formation is modulated along the c axis (that is, perpendicular to the dimer-containing Ir chains). The period of this IC lattice modulation is approximately equal to 10 lattice constants at $T = T_{irr} = 10$ K. X-ray and electron irradiation have the same effect on the CO state in $CuIr_2S_4$. In the both cases, the S peaks disappear, and the dumbbell-shaped diffuse scattering replaces the F peaks in the irradiated state. As an example, dumbbell-shaped diffuse x-ray scattering pattern in the vicinity of the $(5, 5, 4)$ F peak position is shown in Fig. 2.

The long-range order of the Ir dimers is recovered on warming. The recovery is gradual. Figures 2 and 3 show the data taken on warming from $T_{irr} = 10$ K with x rays

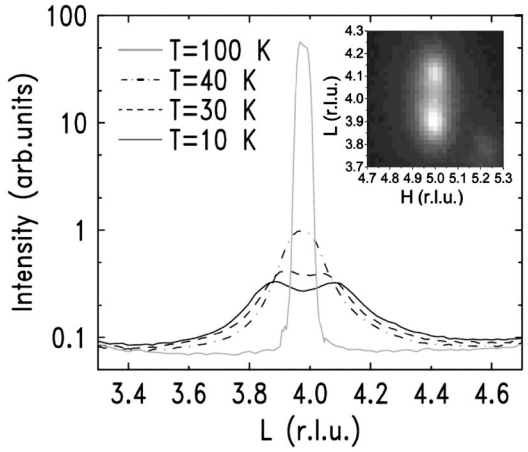

FIG. 2. X-ray scans at the $(5, 5, 4)$ F peak position at various temperatures. The data were taken on warming from $T_{\mathrm{irr}} = 10$ K as described in the text. The inset shows x-ray diffuse scattering pattern in the vicinity of this position at $T = 10$ K. The units for H and L are reciprocal lattice units (r.l.u.)

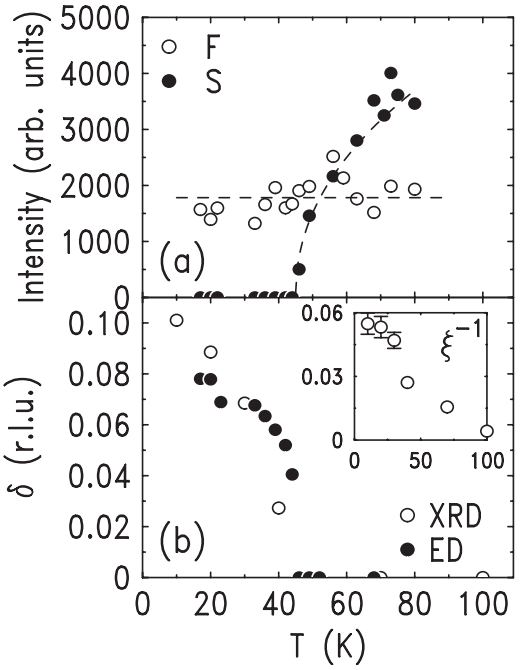

FIG. 3. Temperature dependence of (a) the integrated intensities of the forbidden (F) and the superlattice (S) peaks from ED measurements. (b) Displacement of the scattering maxima from the positions of the commensurate F peaks (the incommensurability of the c-axis lattice modulation) from XRD and ED data. The inset shows the c-axis inverse correlation length of the diffuse peaks from XRD data, in $\mathrm{Å}^{-1}$.

on. The sample was first cooled down from $T = 300$ K with x rays off, and then converted into the IC state as described in Ref. [6]. No time-dependent effects were observed once the temperature was stabilized in each subsequent measurement. As shown in Fig. 2, the two lobes of the dumbbell move closer and finally merge into a single broad peak on warming to $T = 40$ K. Above this temperature, only single broadened peaks at the F positions are observed. These peaks narrow down with the increasing temperature and become resolution limited at $T \approx 100$ K. The temperature dependence of the integrated intensity of the F peaks, the displacement δ of the diffuse peaks from the commensurate position, and the inverse correlation length of the lattice modulation in the c direction are shown in Fig. 3. The correlation length is defined as half width at half maximum of the peak. It was extracted from fits to two Lorentzian peaks for $T < 50$ K and to a single Gaussian peak for higher temperatures.

The data of Fig. 3 show that the ordering of the Ir dimers becomes commensurate for $T > 50$ K, and that the long-range ordered spin-dimerized CO state is restored at $T \approx 100$ K. Importantly, the integrated intensity of the scattering in the vicinity of the F position remains constant in the entire temperature region from 10 to 100 K, as shown in Fig. 3(a). In contrast, the integrated intensity of the S peaks is zero for $T < 50$ K and gradually grows on warming until it reaches the value characteristic to the long-range CO state for $T > 100$ K. These observations strongly support the scenario in which virtually all the Ir dimers are preserved in the radiation-induced state, while the intrachain dimer order as well as the long-range interchain correlations characteristic to the CO state are lost at low temperatures but are recovered on warming [6].

Another important observation is that the nature of the radiation-induced state does not depend on the means of obtaining it. Rather, it depends only on temperature and on the thermal history of the sample. X rays of different energies (6.6–11 keV were tested) and intensity, as well as an electron beam, always produce the same IC state (as defined by the value of δ) at the same temperature. A certain difference in the values of δ of Fig. 3(b) obtained in ED and XRD experiments is likely to be attributed to sample dependence and, perhaps, to imperfect temperature control. This observation strongly suggests that x-ray and electron irradiation reveal intrinsic properties of the low-temperature state of $CuIr_2S_4$.

In the irradiated $CuIr_2S_4$, the conversion of the incommensurate to the commensurate state with increasing temperature is clearly quite unconventional. The behavior of the incommensurability of Fig. 3(b) and of the S peak intensity of Fig. 3(a) suggests that a phase boundary, hidden in the nonirradiated material, might be present at $T \approx 45$ K. Another observation consistent with this scenario is the absence of any x-ray effects for $T_{\mathrm{irr}} > 50$ K. We note, however, that because both the IC and the commensurate x-ray-induced states exhibit only short-range order for $T < 100$ K, various types of temperature-dependent crossover are also possible. Dynamic processes in the metastable disordered state must also be considered to understand this conversion. However, the IC state is stable for at least a few hours with the radiation turned

off for any $T < 45$ K, and therefore these processes are probably of secondary importance.

The observation of changes in the average crystallographic symmetry under irradiation with photons of moderate energy ($E \sim 10$ keV), as in $CuIr_2S_4$ [6], is in itself quite unusual. Electron or ion beams with energies of a few hundred keV and larger are well known to be capable of making structural damage in solids. These beams possess enough energy to produce various lattice defects, often by means of ballistic displacement. Under certain conditions, distinct metastable ordered phases can even be induced. This is observed, for example, in the intermetallic compound Ni_4Mo [12]. X rays of 10 keV, on the other hand, are normally considered a nondamaging probe, and are routinely used for structural analysis. Of course, radiation damage, such as point defect formation, for example, does occur even in this case. However, x-ray irradiation rarely leads to formation of states with new order parameters. Charge-ordered systems, such as $CuIr_2S_4$, provide several prominent exceptions to this rule. In magnetoresistive manganites, for example, x rays convert the CO insulating state into a ferromagnetic metallic (FM) state with less distorted structure [13].

The x-ray effects in $CuIr_2S_4$ differ from these x-ray-induced transitions in one important aspect, however. The most intriguing result of our experiments is the observation of the incommensurate lattice modulation induced by the irradiation. While the newly observed structural correlations are only short range, their existence indicates emergence of a new order parameter in the system. In contrast, in the manganites x rays simply promote a transition from the metastable CO state to the FM state that appears to be the true ground state of this system. Moreover, there are other ways to induce the FM state in the manganites, such as application and subsequent removal of a magnetic field [14]. In $CuIr_2S_4$, on the other hand, a completely new order is induced by the x rays. To our knowledge, this is the first example of such a phenomenon. This observation is even more surprising because any irradiation introduces disorder in the system, and therefore is expected to provide means of destruction of an order, not a way to induce it.

One possible explanation of our results is through a second order parameter, competing with the CO state, that is revealed as the CO state is destroyed by radiation. This can be, for example, an instability against IC lattice modulation such as a CDW. This lattice modulation is likely, in fact, to be short range because it forms on the background of disordered dimers. CDW instabilities due to Fermi surface nesting are indeed quite common in spinels. Examples of CDWs in spinels include CuV_2S_4 and, perhaps, even magnetite [15,16]. Unfortunately, suitable band structure and electronic susceptibility calculations for $CuIr_2S_4$ are not available yet. It was pointed out that full relativistic band calculations with spin-orbit interaction, and inclusion of the electron-phonon interaction are necessary to explore the CDW instability in this material [17]. To test the CDW instability hypothesis for irradiated $CuIr_2S_4$, such calculations are highly desirable. Further experimental work on the mechanism of the irradiation-induced transition is also necessary. While it was suggested that the irradiation results in local destruction of the charge order and subsequent relaxation of the excited electrons into a disordered CO pattern ($CuIr_2S_4$) or even another electronic state (manganites), the detailed mechanism of this transition is still unknown [6,13]. To unravel this mechanism, studies of the effects of the varying radiation energy as well as detailed investigation of the local atomic displacements would be of importance. In addition, systematic application of various time-dependent experimental protocols has to be carried out to understand the nature of the transition at $T = 45$ K and to untangle the effects of temperature variation and the irradiation. These studies will be subject of future work.

In summary, the data presented herein demonstrate that previously unknown incommensurate structural correlations are induced by x-ray photons and moderate-energy electrons in $CuIr_2S_4$. This effect takes place only for T, $T_{irr} < 45$ K, suggesting the presence of a new characteristic temperature in this system. Our observations represent an interesting example of appearance of new order from the irradiation-induced disordered state. We speculate that the observed effects might be explained by existence of an instability (of an unknown nature, thus far) that is suppressed in the CO state, but is revealed as the long-range CO order is destroyed. Therefore, irradiation with x rays or electrons can be used as a tool to reveal otherwise unrealized states in strongly correlated systems.

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