Inhomogeneous Magnetism in Single Crystalline $Sr_3CuIrO_{6+\delta}$: Implications to Phase-Separation Concepts

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The single crystalline form of an insulator, $Sr_3CuIrO_{6+\delta}$, is shown to exhibit unexpectedly more than one magnetic transition (at 5 and 19 K) with spin-glass-like magnetic susceptibility behavior. On the basis of this finding, viz., inhomogeneous magnetism in a chemically homogeneous material, we propose that the idea of "phase separation" described for manganites is more widespread in different ways. The observed experimental features enable us to make a comparison with the predictions of a recent toy model on *magnetic* phase separation in an insulating environment.

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The concept of electronic phase separation has been recently advocated to describe spin-glass-like characteristics induced by disorder in doped manganites and such a state is even thought of as a new state of matter [1]. An important question [1] remaining unaddressed is whether the anomalies characterizing the "phase-separation" phenomenon can be seen even in those *homogeneous* materials (that is, without any additional chemical doping), where there is *no coexistence* of localized and itinerant charge carriers characterizing these manganites. In fact, recently, a toy model was also proposed [2] predicting the role of disorder on the behavior of a system in which any two phases in general, not necessarily of insulator and metal, compete and it is of interest to provide experimental data in different situations to test this theory. In this Letter, we report the magnetic behavior of a pseudo-one-dimensional *insulator* [3–6], Sr_3CuIrO_6, in the single crystalline form. The observed data reveal that the magnetism is of an inhomogeneous nature in these single crystals, with a broad agreement of the experimental features with the predictions of the toy model mentioned above. Hence, we emphasize that the phenomenon of "phase separation"—within the criterion [1] of inhomogeneous magnetism in a homogeneous material—is not restricted to manganites alone.

The compounds of the type, $(Sr,Ca)_3MXO_6$ (M, X = a metallic ion, magnetic or nonmagnetic), crystallizing in the K_4CdCl_6-type rhombohedral structure (space group $R\bar{3}c$), are of considerable importance due to the presence of spin chains (M-X) separated by Sr/Ca ions (see Refs. [3–13], and references cited therein). Among these, in the Cu containing compounds, there is a lowering of the crystal symmetry to monoclinic (space group $C2/c$) due to the Jahn-Teller (JT) effect at the Cu site, a point of importance to the discussion in this article. The readers may see Ref. [7] for more details on crystallographic features.

The single crystals of 3 to 5 mm length and 0.5 to 1 mm diameter were grown [14] by the flux method employing basic alkali fluxes [15]. The crystals were found to undergo monoclinic modification and to grow along the [101] monoclinic axis using single-crystal x-ray diffraction. The lattice constants were found to be $a = 9.298(2)$ Å, $b = 9.714(2)$ Å, $c = 6.710(2)$ Å, and $\beta = 92.19(2)°$. For two orientations of the crystal, viz., $H \parallel [101]$ and $H \perp [101]$, we have measured dc magnetic susceptibility (χ) as a function of T (2–300 K) at different magnetic fields (H = 10, 100, and 5000 Oe) for the zero-field cooled (ZFC) and field cooled (FC) states of the specimens by commercial magnetometers, superconducting quantum interference devices (Quantum Design), as well as vibrating sample magnetometers (Oxford Instruments). In addition, ac χ measurements were performed at low temperatures (2–25 K) at various frequencies.

The T dependence of dc χ below 25 K is shown in Fig. 1 for the ZFC and FC states of the crystal. On comparing the magnitudes of the magnetization for the two different orientations mentioned above, we can conclude that the easy axis of magnetization lies perpendicular to the [101] direction. This is in agreement with the conclusions based on the neutron diffraction pattern of a similar Cu compound [16]. The low-field (H = 10 and 100 Oe) data show that distinct magnetic ordering appears at two temperatures, 5 K (T_1) and 19 K (T_2), the former being much more prominent. The intensity (at low fields) at T_2 is nearly the same for both directions, whereas at T_1 it is markedly enhanced for $H \perp [101]$ as compared to $H \parallel [101]$. This suggests that there is a significant magnetic anisotropy only for the T_1 transition. For comparison, in the same figure we also display the low-field behavior of the polycrystalline form reported earlier [5]. In contrast to single-crystal data, in polycrystals the 19 K transition is very prominent while that at 5 K appears only as a shoulder in the low-field ZFC data; this transition gets more pronounced for moderate values of H [3,5,6]. The fact that this crystal is characterized by more than one magnetic transition is endorsed by similar features in the ac χ data (Fig. 2).

We now address the question of the nature of the magnetic ordering at T_1 and T_2. The real part of ac χ data (Fig. 2) reveals a spin-glass-like frequency dependence with a marginal shift of the curves to higher temperatures with increasing frequency. This is observed for both the

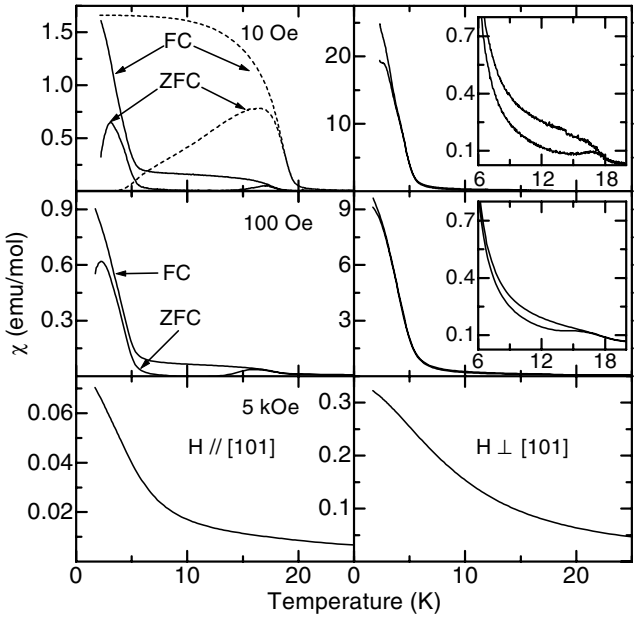

FIG. 1. Temperature dependence of dc magnetic susceptibility below 25 K ($H = 10$, 100, and 5000 Oe) for the ZFC and FC states of single crystalline Sr_3CuIrO_6 for two orientations. The ZFC-FC curves for $H = 5000$ Oe overlap. The data (dashed line) at 10 Oe for the polycrystal from Ref. [5] are included for comparison; note that the values are scaled down by a factor of 20 to accommodate them in the same figure. The insets highlight the 19 K transition.

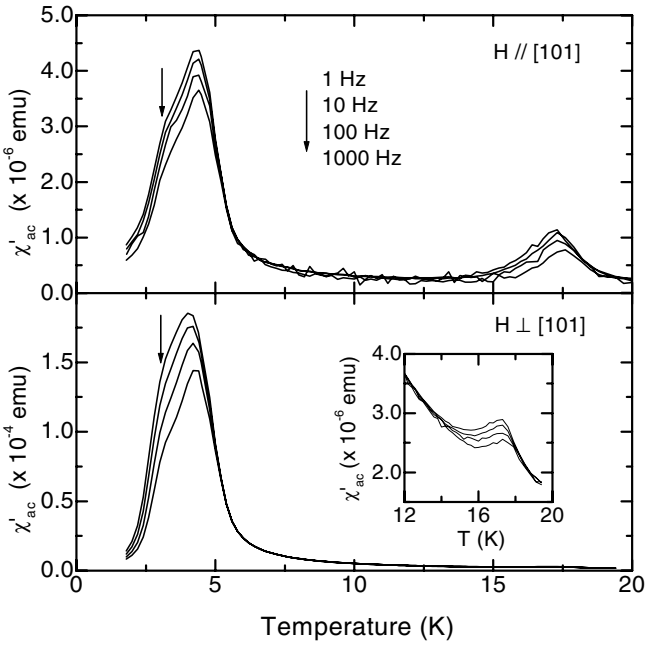

FIG. 2. Real part of ac susceptibility as a function of temperature for two orientations of the Sr_3CuIrO_6 crystal at different frequencies in the region of magnetic ordering. The vertical arrow marks an additional magnetic transition below the peak. The inset (bottom) highlights the 19 K transition.

transitions, implying that the magnetic structure is frustrated both at T_1 and T_2. In support of this, we note that there is a significant difference between ZFC and FC χ vs T curves at low fields for both transitions (Fig. 2). We have also observed a well-defined upturn in the imaginary part of ac χ at these transitions with a similar frequency dependence, a feature typical of only magnetically frustrated systems, and due to space limitations we do not present these data.

The presence of more than one magnetic transition with spin-glass-like behavior is the crucial finding for our main conclusion. It may be noted that all the octahedral (as well as trigonal-prismatic) sites are crystallographically equivalent in the undistorted structure and that spin-glass behavior is not necessarily a favored state as the analogous Zn compound Sr_3ZnIrO_6 (Ref. [6]) is antiferromagnetic (*vide infra*). The reversal of the relative intensity of these two transitions for single crystals when compared with the polycrystalline behavior also clearly excludes the possibility of a single magnetic transition showing progressive spin reorientation effects with a change in temperature. The features attributable to this phenomenon should be intrinsic to the material and should not depend upon single/polycrystalline physical states. The same argument can be given to rule out possible independent ordering of Cu and Ir at T_1 and T_2; this is also inferred from the observation of unequal magnitudes of χ at these transitions even though the spin of each of these ions is $= 1/2$. However, our conclusion is not dependent on whether both these ions order simultaneously or separately (as a given magnetic segment proposed below can contain either of these or both). In view of this situation, we propose that this single crystal could be classified as a *magnetically phase-separated system* [1] in the sense that *there is a coexistence of magnetic-segments, isolated by defects, ordering magnetically at different temperatures.* If these segments are strongly magnetically coupled in a homogeneous manner, one should have expected only one magnetic transition of a long-range type, in contrast to the observations.

This scenario prompts us to view the present finding in light of the predictions of a recent toy model [2], relevant points of which are now briefly outlined. In order to extend the concept of phase separation to situations more general than manganites, Burgy *et al.* [2] explored the consequences of a competition between two ordered states (separated by first-order transition) in the presence of disorder within a toy model; this model does not even assume itinerancy or localization of the carriers and in this sense it is more general. This theory predicts that, below a characteristic temperature, there is an intermediate temperature range with preformed clusters, but with uncorrelated order parameters, giving a globally paramagnetic state; in the lower-T regime, the clusters grow in size, although the disorder is uncorrelated, and percolate upon cooling, eventually resulting in long-range ordering; an application of a small magnetic field should have a dramatic influence on initial isothermal magnetization (M) followed by nonsaturation at higher fields in the event of a competition between ferromagnetic and antiferromagnetic phases.

In light of the above model, we now look at the magnetic behavior of this material, both in polycrystals [5,6] as well as in single crystal (see Fig. 3, top). The plots of inverse χ versus T are found to be nonlinear. One can see this dramatically in single crystals for $H \parallel [101]$ (see Fig. 3, top) in the sense that there is a steep, but gradual, fall of inverse χ below 100 K, though the nonlinearity persists even for the perpendicular direction. This implies varying sizes of the magnetic cluster with decreasing temperature. This increasing intercluster coupling is apparently manifested as a weak magnetic transition at about 19 K in the single crystal, with the rest being paramagnetic at this temperature. The intensity of the response at 19 K, however, must depend upon the number of such clusters. As the disorder in the polycrystalline form is expected to be more, one expects a large number of such independent clusters, and hence the response for the polycrystalline form [5] is relatively large compared to the single crystalline form (see Fig. 1). With a further decrease of T, true bulk ordering develops at about 5 K. There is also a steep increase of M (from zero in zero H) by a small application of magnetic field at 2 K without any saturation at higher fields. These observations are in accordance with the above theory. However, there are some difficulties in claiming that there is total agreement with respect to this model. For instance, (i) we are unable to precisely pinpoint the characteristic temperature, whether it is 100 or 19 K, as the magnetic cluster formation appears to be a continuous process with decreasing temperature and (ii) the magnetic ordering at T_1 appears to be more spin-glass-like, rather than a long-range type. However, we believe such details may be redundant for the present purpose; real systems can behave in a slightly different fashion depending on other complexities (e.g., the degree of disorder, the way the segments grow and couple with a variation of T, crystallographic arrangement, dimensionality, etc.) of the systems. In our case it appears that the competition regime occurs in a more extended T range than assumed by the theory. What is important is that this system catches the essential physics of the model in terms of how the magnetic interaction among the competing "magnetic phases" evolves with decreasing temperature in the presence of disorder in homogeneous material. Finally, we like to stress that this compound is in fact on the verge of long-range magnetic order, as elaborated in Ref. [5], since small applications of H (as low as 1 kOe) depress spin-glass characteristics. This is found to be true for a single crystal as well. Therefore, the discrepancy (ii) is not a serious one and it is of interest to focus future studies to subject this system to other small perturbations (by chemical or external pressure?) to stabilize this long-range magnetic phase, so as to demonstrate the behavior of this system closer to the predictions of the theory.

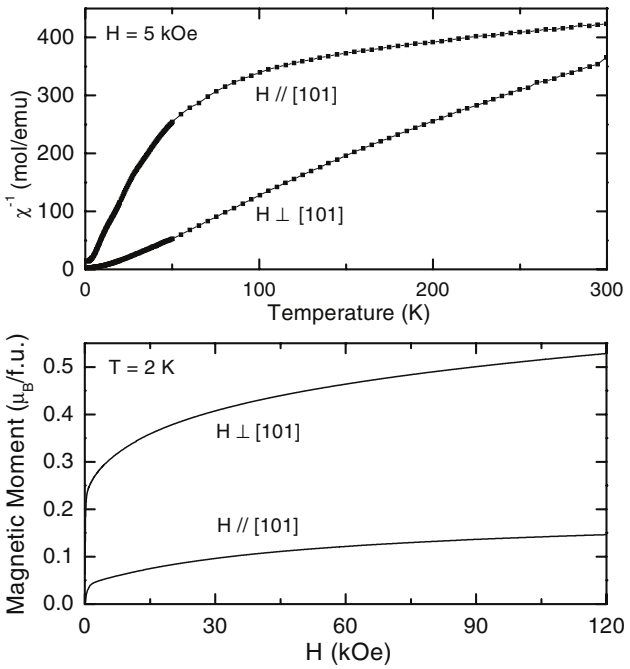

FIG. 3. Inverse susceptibility ($H = 5$ kOe, ZFC) (top) as a function of temperature and isothermal magnetization at 2 K (bottom) for two orientations of the Sr_3CuIrO_6 crystal.

We now briefly discuss how defects (creating segments) can occur in this class of compounds and the reader can see Ref. [17] for details. Apart from vacancies along the magnetic chains, the defects can also arise due to the movement of a small fraction of Sr ions to vacant sites in the chain and it has been shown that the degree of such defects could be tuned by varying synthetic conditions. It has also been established that certain heat treatment conditions increase the oxygen content [5] and the extra oxygen ($0 < \delta < 1$) occupies a trigonal prismatic site, resulting in the conversion of one such site into two octahedral sites. These types of defects are found to occur not only for Cu compounds, but also for Zn/Ni compounds and such "defective" forms have been called "incommensurate" phases. In our earlier polycrystalline studies [5], for the Cu specimens with extra oxygen, the magnetic transition temperature has been found to be lower. For such reasons, we have denoted the oxygen content as "$6 + \delta$" at least at a few places in this article.

Further comparison of the magnetic behavior of this Cu system with the analogous Zn compound, Sr_3ZnIrO_6 (Ref. [6]), is quite intriguing. As mentioned earlier, the Zn compound undergoes long-range magnetic ordering (antiferromagnetic, from Ir ions) at 19 K and the Néel temperature is quite robust to synthetic conditions [5,6], unlike in the Cu compound, in spite of the presence of defects. Therefore, an additional crucial effect must be necessary in the Cu compound to make the magnetism inhomogeneous. As discussed in Ref. [3], the JT active Cu ion results in multiple Cu-Cu and Cu-Ir distances, which we believe is a crucial factor for randomizing magnetic interaction. However, one can also argue that this distortion *alone* may cause a uniform, rather than nonuniform, modification of the nearest neighbor Cu-Cu and Cu-Ir magnetic interaction throughout the crystal. Therefore, we propose

that it is the presence of the defects that somehow separates out islands of magnetic ions (phase separation) of a given exchange interaction strength following JT distortion. We welcome future experiments to verify this conjecture.

Various other interesting observations arise from our measurements. (i) The peak in the low-field ZFC dc χ data at about 3 K vanishes at a higher field (5 kOe), as does the ZFC-FC bifurcation. This implies complex thermomagnetic history effects on magnetism even in single crystals. (ii) The saturation moment (at 2 K) obtained by linear extrapolation of the high-field data (60–120 kOe) to zero field even for H parallel to easy axis ($\sim 0.4\mu_B$ for $H \perp [101]$) is much lower than that expected for ferromagnetically coupled Ir and Cu ($S = 1/2$) ions (see Fig. 3, bottom). The reduced value implies the existence of a moment-compensation effect, e.g., the magnetic frustration among the segments/chains. This behavior is the same as in polycrystals [5]. Further evidence for frustration was presented earlier [5], e.g., by the absence of a heat-capacity anomaly at the transition. (iii) The ac χ data for $H \parallel [101]$ reveal that there are at least two transitions below 5 K separated by about 1 K, with the vertical arrow in Fig. 3 marking one transition and the peak representing another transition. A careful inspection of the ZFC dc χ data at low fields also reveals the existence of a shoulder at a temperature slightly above the peak. These observations suggest that one gets additional transitions at different temperatures depending upon the size of the segments regulated by defects/disorder as pointed out by Dagotto *et al.* [1]. We find that the relative contribution to χ for the two closely spaced transitions near T_1 is also a sensitive function of H, as revealed by reversal of the peak positions in dc and ac χ plots. In addition, the transitions at T_1 and T_2 broaden upon application of a higher field (5 kOe) (Fig. 1), indicating strong field-induced intersegment coupling effects. (iv) For $H \parallel [101]$, for the ZFC data at low fields, the value of χ for $T_1 < T < T_2$ is negligibly small, indicating near-compensation of the magnetic moments among the segments. This behavior too is modified by changing the history of the sample (FC, higher fields, etc.). All these observations, revealing the sensitivity of magnetically separated segments to the magnetic field, history effects, etc., may be useful for further refinement of theoretical formulations.

To conclude, we have observed distinct evidence for inhomogeneous magnetism in single crystalline $Sr_3CuIrO_{6+\delta}$, on the basis of which the idea of phase separation for a chemically homogeneous insulating medium is proposed. Presumably, an interplay between the Jahn-Teller effect and the defects is required to result in inhomogeneous magnetism in this material. We have argued that this material apparently serves as a favorable testing ground for a recent toy model of phase separation [2] in an insulating environment. It will be very fascinating if there is a consensus on the type of phase separation proposed in this article, since unlike in manganites, (i) there is no coexistence of localized and itinerant magnetic species and (ii) the magnetic phases are produced without involving any chemical doping. In this sense, the root cause of spin-glass-like anomalies in this system is different from that in other conventional spin-glasses in which chemical substitution is required for randomizing exchange coupling. In view of this, we offer an explanation to a question raised [1] in this regard: In which way are phase-separated materials different from spin-glasses? In our opinion, it is the "cause" which is responsible for the "result" that makes the former fundamentally different from the latter. Finally, we hope that this article triggers more work on spin-chain oxides with this crystal structure.

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