

# Magnetic anomalies in the spin chain system, $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$

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We report the results of ac and dc magnetization (M) and heat-capacity (C) measurements on the solid solution,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ . While the Zn end member is known to form in a rhombohedral pseudo one-dimensional  $\text{K}_4\text{CdCl}_6$  structure with an antiferromagnetic ordering temperature of ( $T_N =$ ) 19 K, the Cu end member has been reported to form in a monoclinically distorted form with a Curie temperature of ( $T_C =$ ) 19 K. The magnetism of the Zn compound is found to be robust to synthetic conditions and is broadly consistent with the behavior known in the literature. However, we find a lower magnetic ordering temperature ( $T_o$ ) for our Cu compound ( $\sim 13$  K), thereby suggesting that  $T_o$  is sensitive to synthetic conditions. The Cu sample appears to be in a spin-glass-like state at low temperatures, judged by a frequency dependence of ac magnetic susceptibility and a broadening of the C anomaly at the onset of magnetic ordering, in sharp contrast to earlier proposals. Small applications of magnetic field, however, drive this system to ferromagnetism as inferred from the M data. Small substitutions for Cu/Zn ( $x=0.75$  or  $0.25$ ) significantly depress magnetic ordering; in other words,  $T_o$  varies non-monotonically with  $x$  ( $T_o \sim 6, 3$  and  $4$  K for  $x=0.25, 0.5,$  and  $0.67$  respectively). The plot of inverse susceptibility versus temperature is non-linear in the paramagnetic state as if correlations within (or among) the magnetic chains continuously vary with temperature. The results establish that this class of oxides is quite rich in physics.

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The investigation of compounds with low-dimensional crystallographic features has gained considerable momentum in recent years, following a variety of physical phenomena such systems are found to exhibit. For instance, the magnetic systems of low dimensionality with integer spins and non-integer spins are expected to behave differently in the sense that the former exhibits a (Haldane) gap, while latter type does not.<sup>1</sup> It is therefore worthwhile to identify new systems with low dimensional structural features and to subject them to intense investigations.

In this regard, the compounds of the type,  $\text{A}_3\text{MXO}_6$  ( $A = \text{Ca, Sr, Ba}$ ;  $M =$  a magnetic or a non-magnetic ion;  $X =$  a magnetic ion) are of considerable interest (see, for instance, Refs 2-20), as this class of compounds crystallize in a rhombohedral structure of  $\text{K}_4\text{CdCl}_6$  type (space group  $\text{R}\bar{3}\text{c}$ ) characterized by the presence of pseudo-one dimensional chains of M-X along c-direction; the structure consists of infinite chains of alternating face-sharing  $\text{MO}_6$  trigonal prisms and  $\text{XO}_6$  octahedra; the one-dimensional character can be expected under favor-

able conditions (that is, if intra-chain magnetic ion separation is shorter than that of interchain) as these chains are separated by non-magnetic A ions. The ions at the M and X sites are generally different, except the case of Co which occupies both the sites simultaneously, e.g.,  $\text{Ca}_3\text{Co}_2\text{O}_6$  (Ref. 11). Both M and X can be magnetic ions or M can be a non-magnetic ion (like Li, Na, K), while X can be a magnetic-moment carrying ion. The variety of substitutions at these two sites (M and X) this structure offers provide interesting opportunities to tune interchain and intrachain interactions by selective substitution by a magnetic or a non-magnetic ion at the M site, resulting in different types of magnetic structure.

We believe that this class of compounds have not been sufficiently studied in spite of the fact that the reports available to date reveal interesting anomalies: For instance, the series  $\text{Sr}_3\text{CuPt}_{1-x}\text{Ir}_x\text{O}_6$ , in which initially random quantum spin chain paramagnetism was proposed for  $x=0.5$ , has been found to exhibit more complex magnetism.<sup>15,16</sup> Zn in  $\text{Sr}_3\text{ZnIrO}_6$  exists in an unusual trigonal prismatic coordination.<sup>13</sup> Co present at the two sites (with high and low spin) possesses different magnetic moments exhibiting multiple sharp transitions in the isothermal magnetization (M) data.<sup>11</sup> Magnetic ordering is seen for 4d and even for 5d ions (like Pt, Ir, Rh), and particularly noteworthy is that Ru (at the X site) exhibits magnetic ordering at an unusually large temperature (about 110 K) with both ferromagnetic and antiferromagnetic-like features in the M data.<sup>3,4,18,19</sup> In addition, due to Jahn-Teller effect of the Cu ions (at the M site), for Cu containing compounds, the one-dimensional structure is not that of a simple collinear chain. For instance, in  $\text{Sr}_3\text{CuIrO}_6$ , the Ir ions lie on a straight line, whereas the  $\text{Cu}^{2+}$  ions are offset from the chain axis toward one of the faces of the oxygen trigonal prism by  $0.53 \text{ \AA}$  resulting in a pseudosquare planar coordination; the direction of offset rotates by  $180^\circ$  from one Cu atom to the next along the chain. These displacements of atoms result in a monoclinic distortion (space group  $\text{C}2/c$ ) of the structure.<sup>21</sup> It is thus clear that these oxides exhibit a variety of interesting magnetic and crystallographic features and it is therefore of interest to carry out a systematic study of these compounds. We have earlier reported interesting magnetic anomalies in Ru based compounds<sup>18,19</sup> and, as a continuation of our studies in this direction, we have carried out magnetic investigations on the oxides,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ .

The investigation of the present Cu-Zn based solid solution was primarily motivated by interesting magnetic

anomalies in the solid solution  $\text{Sr}_3\text{CuPt}_{1-x}\text{Ir}_x\text{O}_6$  (Ref. 15,16) due to coexisting ferro and antiferro-magnetic interactions within the chain. There are considerable theoretical interests on the thermodynamics of systems with random ferromagnetic-antiferromagnetic chains<sup>22</sup> in the current literature and therefore it is worthwhile to identify such systems. The Cu and Zn end members in the present solid solution have been previously reported to order essentially ferro and antiferromagnetically respectively close to 19 K.<sup>13,14,15,16</sup> Therefore, this solid solution is expected to provide an opportunity to probe the magnetic behavior by disruption of the magnetic chains by substitution of Zn for Cu. Apart from throwing light on the magnetism of end members, we observe many interesting anomalies in our measurements which are reported in this article.

The samples,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ , ( $x= 0.0, 0.25, 0.5, 0.67, 0.75$  and  $1.0$ ), were prepared by a conventional solid state reaction method. The stoichiometric amounts of high purity ( $> 99.9\%$ )  $\text{SrCO}_3$ , Ir metal, CuO and ZnO were intimately mixed under acetone and preheated at  $800^\circ\text{C}$  for 33 hours. These were thoroughly ground again, pelletized and sintered at  $1150^\circ\text{C}$  for 100 hours with three intermediate grindings. The samples were characterized to be single phases by x-ray diffraction (Cu  $K_\alpha$ ). Rietveld refinement of the x-ray data using DBWS-9411 (Ref. 23) yielded the monoclinic structure for  $x= 0.0$  (as reported earlier) and  $0.25$ . This is also evident from the splitting of some of the lines (see, for instance, the lines falling in range  $42$  to  $46$  degrees in Fig. 1). For  $x \geq 0.5$ , the monoclinic distortion disappears and the patterns could be satisfactorily fitted within the rhombohedral structure. The lattice constants derived from the refinement are included in Fig. 1 and the values for the end members agree with the literature.

We have measured dc magnetic susceptibility ( $\chi$ ) as a function of temperature ( $T= 2-300$  K) at different magnetic fields ( $H$ ) and isothermal magnetization ( $M$ ) at  $2$  K, by a commercial superconducting quantum interference device (Quantum Design) as well as a vibrating sample magnetometer (Oxford Instruments). In addition, ac  $\chi$  measurements were performed in the vicinity of the magnetic ordering temperature ( $T_o$ ) at various frequencies. Heat-capacity ( $C$ ) measurements ( $2-40$  K) were performed by a semi-adiabatic heat-pulse method.

We first discuss the observations on the end members. With respect to  $\text{Sr}_3\text{CuIrO}_6$ , we display low  $T$  dc  $\chi$  in figure 2. It is distinctly clear that there is a sharp rise of  $\chi$  below  $13$  K for the data recorded at different fields indicating the onset of magnetic ordering. However, the observed  $T_o$  is significantly lower than that reported ( $19$  K) in the literature.<sup>15,16</sup> In order to resolve this issue, we prepared another batch of sample (batch 2) with the same heat treatment conditions, however with a reduced duration of hours of sintering ( $1150^\circ\text{C}$ ,  $72$  hours with three intermittent grindings); and we noticed<sup>24</sup> that the value of  $T_o$  now agrees with that of literature. This clearly establishes that  $T_o$  is sample dependent for this com-

position and prolonging the heat-treatment well beyond 24 hours (after each grinding) depresses  $T_o$  - a fact not known earlier in the literature. We have confirmed this observation by repeated preparation of samples. A slight reduction ( $5\%$ ) in Cu in the starting stoichiometry also modifies  $T_o$  in the same way.<sup>24</sup> In order to further understand the origin of this sample dependence, we have carried out energy dispersive x-ray (EDX) analysis. We notice that the atomic ratios of metallic components are very close to the stoichiometry, but O contents are different in these two specimens; batch 1 (the batch discussed in this article) contains excess oxygen (close to atomic ratio  $7$ ), while in batch 2, O content is close to the ratio  $6$ . It is therefore clear that prolonged heat treatment results in excess oxygen intake, resulting in a depression of  $T_o$ . It is of interest to focus future studies on the site of extra oxygen.

With respect to the nature of the magnetic ordering, a plot of inverse  $\chi$  versus  $T$  at low temperatures (below  $30$  K, Fig. 3) extrapolates to a positive value of paramagnetic Curie temperature ( $\Theta_p$ ) as if the compound undergoes ferromagnetic ordering. However, a look at the frequency dependence of ac  $\chi$  (Fig. 4), is quite revealing. Not only the peak height, but also the peak temperature in the ac  $\chi$  data is found to be highly sensitive to frequency, shifting it upwards by as much as  $1.6$  K as the ac frequency is increased from  $3$  to  $1000$  Hz. This property implies that this compound behaves like a spin-glass, in sharp contrast to earlier proposals in the literature. This frequency dependence is relatively less (about  $0.5$  K) for the batch 2 specimen.<sup>24</sup> Interestingly, this frequency dependence vanishes by the small application of an external dc magnetic field (say,  $1$  kOe). We interpret, therefore, that the spin-glass-like state turns to ferromagnetic ordering by the presence of a small magnetic field. The dc magnetization behavior at  $2$  K, in fact, establishes field-induced ferromagnetism of this compound (Figs. 5 and 6). A careful look at the hysteresis loops (Fig. 5) at  $2$  K suggests that the initial virgin curve is not typical of perfect ferromagnets as there is a flat region for  $H < 500$  Oe before  $M$  rises sharply, followed by saturation at higher fields. This finding endorses that there is actually an antiferromagnetic component in zero-field. Though domain wall pinning effects also can give rise to initial flattening of  $M$  vs  $H$  plot, this possibility is ruled out considering that the virgin curve in the hysteresis plot deviates from the center of the hysteresis loop. Another noteworthy feature (Fig. 2) in the magnetically ordered state is that, there is a peak at about  $9$  K in the plot of zero-field-cooled (ZFC) dc  $\chi$  versus  $T$  for  $H= 10$  Oe decreasing to relatively insignificant values of  $\chi$  at about  $2$  K. This peak shifts to a lower temperature ( $5$  K) for  $H= 100$  Oe. Higher applications of  $H$  (say,  $5$  kOe) wipe out the drop in  $\chi$  at low temperatures. The field-cooled (FC) curves, however, do not show this anomaly for any value of  $H$ . Clearly, there is an interesting magnetic anomaly well below  $T_o$  which is history/field dependent. Such low temperature anomalies were reported even in the ac

$\chi$  data earlier.<sup>16</sup> It is worthwhile to focus future studies on this feature.

Other important observations for the Cu sample are: (i) The isothermal M, subsequent to a steep rise around 300 Oe, undergoes a very weak rise at higher fields (Fig. 6). The saturation moment value, derived from the linear extrapolation of the high field M data to zero field is much smaller (close to  $0.35 \mu_B$ ) than that expected if one assumes ferromagnetically-coupled spin 1/2 at both Cu and Ir sites. This value is also smaller than that of the effective moment ( $\mu_{eff} = 2.5 \mu_B$  per formula unit) obtained from the paramagnetic high temperature (200–300 K) linear region of the inverse  $\chi$  vs T plot. This observation, agreeing with that of Ref. 16, suggests that interchain interaction could be antiferromagnetic. (ii) The plot of inverse  $\chi$  versus T in the entire range of the paramagnetic state (Fig. 3) is found to be highly non-linear. Since these compounds are insulators, such a non-linearity cannot arise from (temperature independent) Pauli paramagnetic contribution. This interesting finding therefore is attributed to variation of the effective coupling with changing T. This implies the formation of uncoupled magnetic segments<sup>24</sup> along the chain, probably isolated by disorder/vacancies at rather high temperatures in the paramagnetic state. We also note that the degree of the curvature decreases (Fig. 3, see curve 0.0 b) if one takes excess CuO (say, 10%) in the starting stoichiometry, thereby establishing the role of vacancies in the stoichiometric material on the  $\chi$  behavior discussed above. (iii) The FC and ZFC  $\chi$  curves begin to deviate just above the peak temperature, a characteristic feature in spin-glasses. (iv) The anomaly normally expected due to magnetic ordering at  $T_o$  in the plot of C versus T is absent (Fig. 7), which is a characteristic of spin-glasses as well.

In sharp contrast to the behavior of the Cu sample, the Zn sample is found to be more robust both to slight deviations in stoichiometry as well as to heat treatment conditions. Both the batches (1 and 2) of the stoichiometric samples prepared under the same conditions as the Cu samples exhibit similar magnetic behavior: There exists a well-defined peak in  $\chi$  at about 20 K (Fig. 2), similar to that reported earlier.<sup>16</sup> There is a weak rise with decreasing T at low temperatures in our data which could arise from paramagnetism of the moment-carrying Ir ions at the free ends of the segments. We observe neither frequency dependence of ac  $\chi$  nor significant differences in ZFC-FC dc  $\chi$  curves, unlike in the Cu sample, establishing that this compound is not a spin-glass. In fact, the isothermal M at 2 K undergoes linear variation with H till the highest field measured (120 kOe), indicating that the Zn end member undergoes long range antiferromagnetic ordering, clearly from Ir ions. There is some degree of non-linearity in the plot of inverse  $\chi$  versus T in the paramagnetic state (Fig. 3), the curvature of which gets reduced if one takes 10% excess ZnO in starting composition. This endorses our view stated above that vacancies along the chain cause this effect. The  $\Theta_p$

(in the range 30–50 K) is found to be negative with the same magnitude as that of  $T_o$  and thus both the sign and the magnitude are in full agreement with the proposal of antiferromagnetic ordering in this compound. The value of  $\mu_{eff}$  obtained from the linear region ( $1.6 \mu_B$ ) agrees with that reported earlier.<sup>16</sup> It should also be noted that there is a very prominent anomaly in C in the vicinity of magnetic ordering (Fig. 7), unlike in the Cu sample, which establishes long range magnetic ordering in this compound.

It is quite instructive to see how the magnetism evolves as Cu is gradually substituted for Zn. For this purpose, we present here the results of our investigations on the compounds,  $x = 0.25, 0.5, 0.67$  and  $0.75$  (batch 1) and the findings are found to be qualitatively similar even for those prepared in batch 2. For  $x = 0.75$ , it is interesting to see that the  $\chi$  (both dc and ac) undergoes a monotonic increase with decreasing temperature, as though there is no magnetic ordering down to 2 K. There is no frequency dependence of ac  $\chi$  as well in the T range of investigation. However, in the dc  $\chi$  data, there is a marginal change in slope around 7 K (marked by a vertical arrow in Fig. 2), a feature which is confirmed for repeated preparation of samples. In order to probe the origin of this feature, we have measured C and the data (Fig. 6) shows a weak, but noticeable drop around 7 K. This indicates an onset of weak magnetic order below 7 K. Considering the trends in ac  $\chi$  data discussed above, the magnetic ordering is not even of a spin-glass type, which is also endorsed by the absence of a bifurcation of ZFC-FC  $\chi$  curves. It is possible that this signals incipient antiferromagnetism for this composition, considering that the next higher Zn composition is antiferromagnetic. In any case, it is clear that  $T_o$  is depressed significantly by small substitutions of Cu/Zn, which could be due to local magnetic frustration effects due to substitution of Cu for Zn. In fact, a careful look at the plot of M versus H (Fig. 6) suggests that the linearity observed for Zn end member is absent for this composition and the plot exhibits a curvature as though there is a ferromagnetic component. However, the plot is still non-hysteretic. It is also worth noting that the inverse  $\chi$  (Fig. 3) is non-linear - a feature incidentally maintained for all the solid solutions. Clearly, a small replacement of Cu for Zn brings out dramatic changes in the magnetic characteristics.

Upon further replacement of Zn by Cu, say  $x = 0.67$ , we observe features due to magnetic ordering in the  $\chi$  data, however only at a low temperature. The ZFC  $\chi$  curve exhibits a broad peak around 3 K with the ZFC-FC curves bifurcating below 4 K. The ac  $\chi$  data also show a tendency to flatten below 4 K without any noticeable frequency dependence. The behavior of isothermal M at 2 K is qualitatively similar to that of  $x = 0.75$ . On the basis of M behavior, one can infer that this compound undergoes magnetic ordering of a canted-moment type.

For  $x = 0.5$ , there is a very distinct peak at 3 K in ac  $\chi$  data, undergoing an upward shift with increasing frequency - a feature vanishing for small applications of H,

say 1 kOe, as in the case of the Cu end member. There are corresponding anomalies in the plot of dc  $\chi$  versus T plot as well: The ZFC-FC curves deviate from each other below  $T_o$ . We infer that Cu-end-member-like behavior sets in at this composition, though  $T_o$  is reduced. In contrast to the behavior of the compositions with lesser Cu content discussed above, M at 2 K rises rather sharply at low fields with a curvature towards saturation, though it continues to rise till the high fields measured (Fig. 6). This observation also suggests the existence of a strong competition from ferromagnetic correlations. It may be better to classify this composition as a magnetically frustrated system, considering the absence of a well-defined prominent peak in the C data around 3 K; a weak drop below 3 K is not characteristic of magnetic systems exhibiting long range order.

For  $x=0.25$ , the features in ac and dc  $\chi$ , isothermal M, hysteresis and the C data are similar to that of  $x=0.0$ , except that the magnetic ordering appears below 6 K, and this compound appears to be spin-glass-like in zero-field; this value of  $T_o$  also establishes that a small disruption of the chain depresses magnetism at the Cu end as well.

Summarizing, we have performed magnetic measurements on an interesting class of oxides exhibiting quasi-one-dimensional structural characteristics. We emphasize on the following findings: (i) The Cu end member exhibits spin-glass-like characteristics in the ac  $\chi$  data in zero magnetic field, which reveals that the exchange interaction is actually three-dimensional and not one-dimensional at least in the magnetically ordered state, since in one-dimension it is rather difficult to visualise spin-glass freezing. (ii) The spin-glass-like features are observed for all  $x < 0.5$  and an application of a magnetic field drives this state towards a ferromagnetic state with a reduced moment.<sup>25</sup> (iii) For the Cu end, the  $T_o$  is found to be sensitive to the preparative conditions of the specimens presumably due to the deviations in oxygen/Cu stoichiometry. However, the Zn end member does not exhibit such a sensitivity of magnetism on the preparative conditions and thus the antiferromagnetism observed in this compound is rather robust. (iv) The  $T_o$  is found to undergo a sharp dip for small substitutions of Cu/Zn and thus exhibits non-monotonic variation with  $x$ , implying strong competition between ferromagnetic and antiferromagnetic interactions in the solid solution. (v) The absence of Curie-Weiss behavior of  $\chi$  in the paramagnetic state in the entire solid solution indicates the existence of paramagnetic segments which are isolated from each other due to the disruption of chains by disorder, with drastic changes in the effective magnetic couplings among these segments with varying temperature. The results reveal the existence of an interesting T-H-x magnetic phase diagram for  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ , establishing richness in the physics<sup>26,27</sup> of these compounds.

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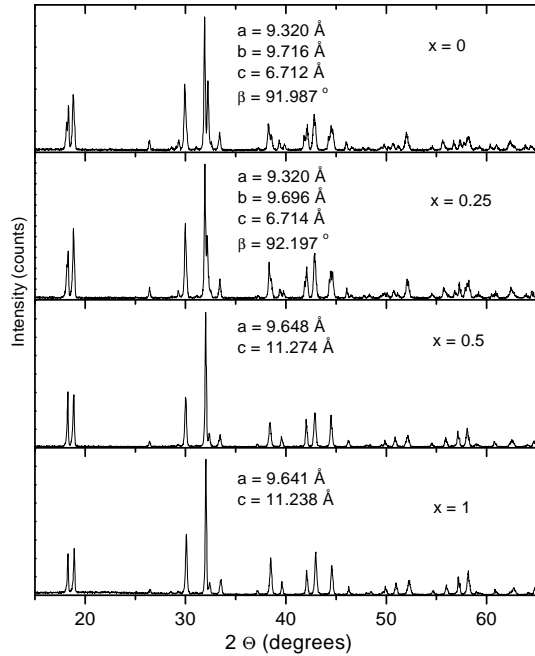


FIG. 1. X-ray diffraction pattern ( $\text{Cu } K_{\alpha}$ ) for the compounds of the series,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ . For  $x > 0.5$ , the patterns are similar and hence not shown for all compositions. For  $x = 0.0$  and  $0.25$ , monoclinic distortion leads to the splitting of the lines, which is clearly resolved for the most intense line and the ones in the range  $42$  to  $46$  degrees.

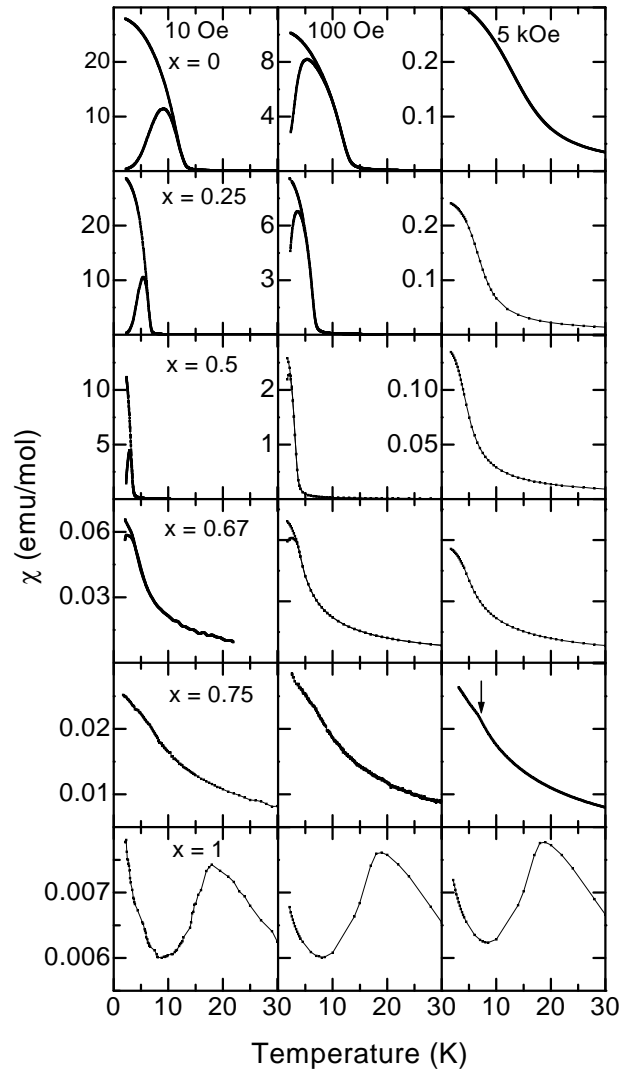


FIG. 2. Temperature dependence of dc magnetic susceptibility ( $\chi$ ) below  $30$  K measured in the presence of different magnetic fields ( $10$ ,  $100$  and  $5000$  Oe) for the zero-field-cooled (ZFC) and field-cooled (FC) states of the specimens,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ . The vertical arrow marks the temperature at which there is a sudden change in slope for  $x = 0.75$ . The plots in a given row are pertinent to one composition.

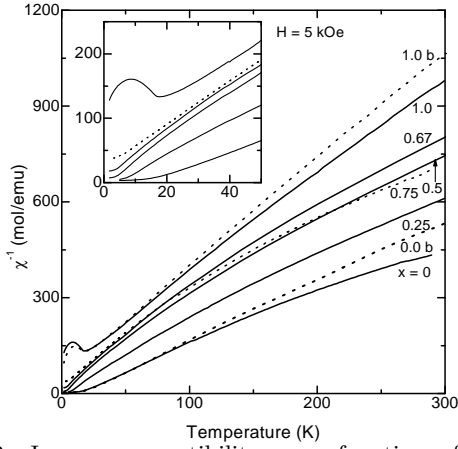


FIG. 3. Inverse susceptibility as a function of temperature measured in the presence of a magnetic field of 5 kOe for all the compositions of the series,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$  (zero-field-cooled state). The data labelled, 0.0 b and 1.0 b, shown by dotted lines corresponding to Cu and Zn end members with 10% excess CuO and ZnO respectively in the stoichiometry, are also shown to highlight reduced curvature of the plots in the paramagnetic state for these compositions. The insets show the data for  $T < 50$  K for all the compositions (except those with excess CuO/ZnO) to highlight the sign and the magnitude of the Curie-Weiss parameter at low temperatures.

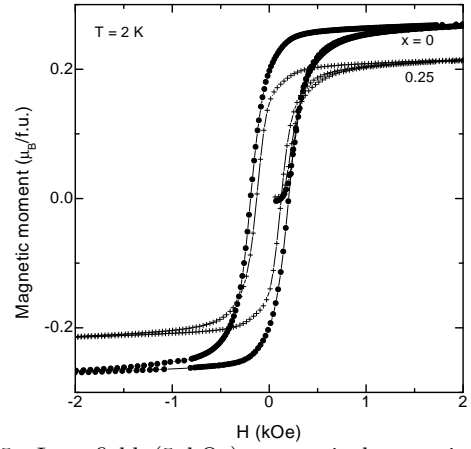


FIG. 5. Low field (5 kOe) magnetic hysteresis loops at 2 K for two compositions  $x = 0.0$  and  $0.25$  in the series,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ . Since no hysteresis has been observed for other compositions, the corresponding curves are not being shown here.

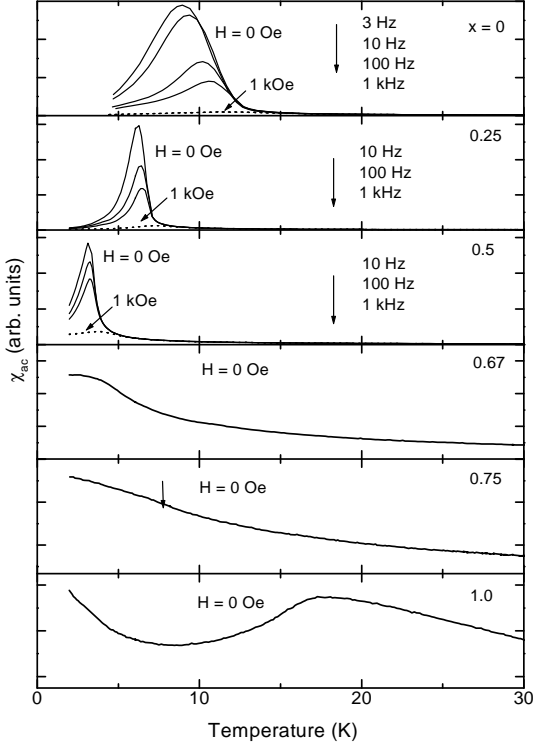


FIG. 4. Real part of ac susceptibility as a function of temperature for the series,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$  at different frequencies. The plots at different frequencies for  $x = 0.67, 0.75$  and  $1.0$  overlap. For  $x = 0.0, 0.25$  and  $0.5$ , the curves are shown also in the presence of a magnetic field of 1 kOe and these at different frequencies overlap with each other.

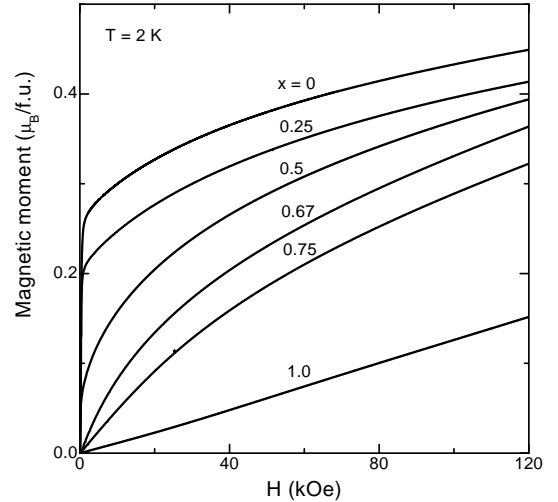


FIG. 6. Isothermal magnetization at 2 K as a function of magnetic field up to 120 kOe for all the samples of the series,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ .

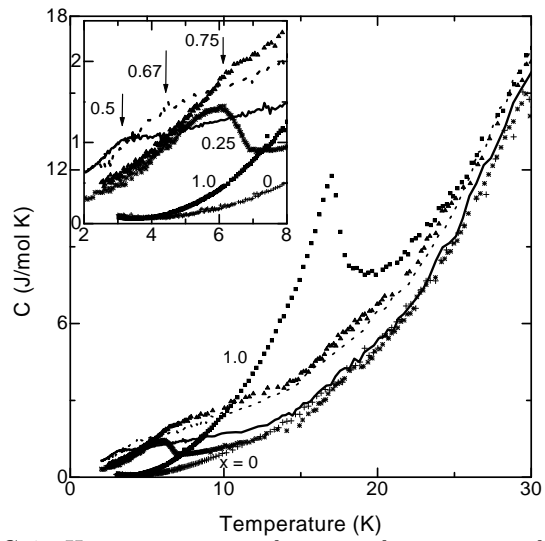


FIG. 7. Heat capacity as a function of temperature for the series,  $\text{Sr}_3\text{Cu}_{1-x}\text{Zn}_x\text{IrO}_6$ . The inset shows the data at low temperatures in an expanded form so as to highlight the weak features (marked by vertical arrows) in some cases due to magnetic ordering.