

## The growth of a single crystal of $\text{Sr}_3\text{CuIrO}_6$ and its magnetic behavior compared to polycrystals

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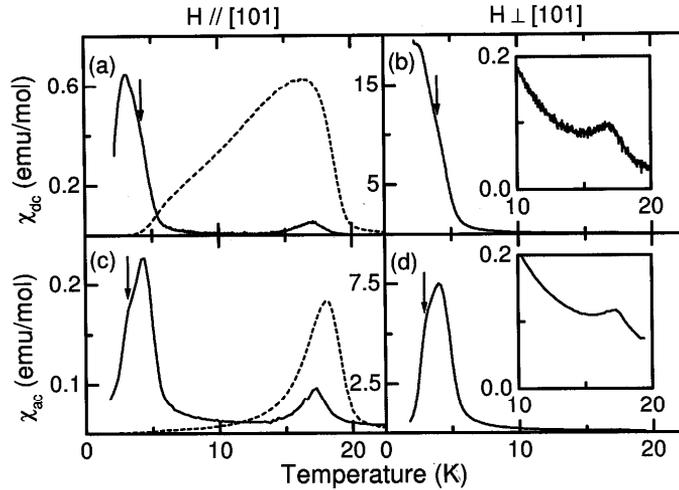
**Abstract.** We have grown single crystals of the pseudo-one-dimensional compound  $\text{Sr}_3\text{CuIrO}_6$ , a  $\text{K}_4\text{CdCl}_6$ -derived monoclinic structure with Cu–Ir chains along the [101] direction. We present the ac and dc magnetization behavior of the single crystals in comparison with that of the polycrystalline form reported earlier. There is a distinct evidence for at least two magnetic transitions, at 5 K ( $T_1$ ) and 19 K ( $T_2$ ), with different relative magnitudes in the single and polycrystals. The low temperature magnetic relaxation behavior of both the forms is found to be widely different, exhibiting unexpected time dependence.

**Keywords.** Magnetic behavior; single crystal  $\text{Sr}_3\text{CuIrO}_6$ ; spin chains.

**PACS No.** 75.30.-m

### 1. Introduction

The compounds of the type  $(\text{Sr}/\text{Ca})_3\text{MXO}_6$  ( $M$  = a metallic ion, magnetic or non-magnetic), crystallizing in the  $\text{K}_4\text{CdCl}_6$ -type rhombohedral structure (space group  $R\bar{3}c$ ), have been attracting attention due to the presence of spin chains ( $M$ -X) separated by Sr/Ca ions [1–4]. The chains consist of face-sharing of octahedra of X ions and trigonal prisms of M ions. Among these, compounds containing the Jahn–Teller (J–T) active Cu are crystallographically of special interest. In  $\text{Sr}_3\text{CuIrO}_6$ , while Ir ( $S = 1/2$ ) occupies the octahedral site, the trigonal prismatic site containing Cu ( $S = 1/2$ ) undergoes J–T distortion with Cu displaced towards one of the rectangular faces. The direction of offset rotates by  $180^\circ$  from one  $\text{Cu}^{2+}$  ion to the next along the chain, resulting in zig-zag Cu–Ir–Cu chains. Consequently, the crystal symmetry is lowered to monoclinic ( $C2/c$ ). We have recently reported some sample dependent magnetic anomalies in the polycrystalline form of this material [1]. We have now grown single crystals of this compound and observe contrasting magnetic behavior in single crystals as compared to the polycrystalline form.

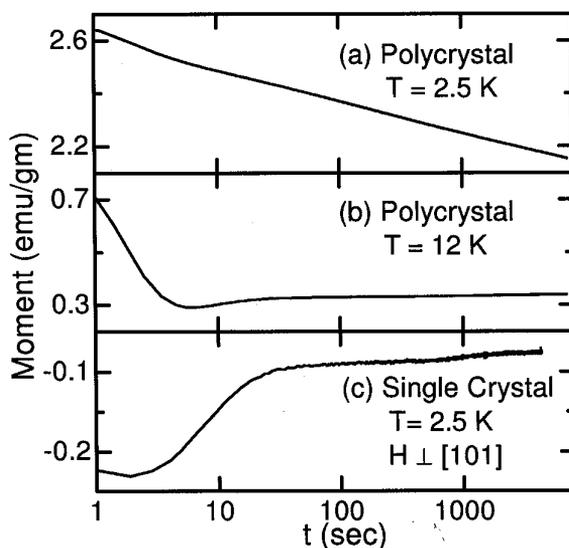


**Figure 1.** Temperature dependence of zero-field cooled  $\chi$  below 25 K for  $\text{Sr}_3\text{CuIrO}_6$ . Parts (a) and (b) show  $\chi_{dc}$  ( $H_{dc} = 10$  Oe); (c) and (d) show  $\chi_{ac}$  ( $H_{ac} = 1$  Oe, frequency = 1 Hz). Solid curves are single crystal data: (a) and (c) for  $H \parallel [101]$ ; (b) and (d) for  $H \perp [101]$ . Dashed curves are polycrystal data [1] scaled down by a factor of (a) 25 and (c) 50, respectively. The insets in (b) and (d) magnify the  $T_2$  transition for  $H \perp [101]$ .

## 2. Experiment

The single crystals, 3–5 mm long and 0.5–1 mm in diameter, were grown by the flux method employing basic alkali fluxes [5] as follows: Stoichiometric amounts of CuO and Ir and twice the stoichiometric amount of  $\text{SrCO}_3$  were thoroughly ground and placed in an alumina crucible. On the top of this mixture, dried  $\text{K}_2\text{CO}_3$ , which is 20 times in weight compared to the mixture, was placed. The crucible was covered with a ceramic plate and subjected to the following heat treatment in air: 30°C to 850°C at the rate of 10°C/min, then to 1100°C at the rate of 1°C/min, held at 1100°C for 3 days, cooled slowly (0.1°C/min) to 850°C and then rapidly to room temperature. Subsequently, the crucibles were placed in a beaker of hot distilled water for several hours and the crystals were carefully separated. The material was further cleaned in a saturated ammonium chloride solution ultrasonically. Single crystal X-ray analysis confirmed the monoclinic structure with lattice constants  $a = 9.298(2)$  Å,  $b = 9.714(2)$  Å,  $c = 6.710(2)$  Å and  $\beta = 92.19(2)^\circ$ , which agree well with the data from literature [6]. The rod-shaped crystals grow along the monoclinic [101] axis, which in these linear chain compounds is also the Cu–Ir–Cu chain axis. The rhombohedral-derived crystal structure can also be transformed to a pseudo-hexagonal cell ( $a_1 = 9.7142$  Å,  $a_2 = 9.625$  Å,  $c = 11.256$  Å,  $\alpha_1 = 90.35^\circ$ ,  $\alpha_2 = 89.96^\circ$  and  $\gamma = 120.3^\circ$ ). However, the true structure is monoclinic and further discussions henceforth in this article are with respect to this structure are given here [5].

The magnetic measurements were carried out for two orientations of the external field with respect to the principal crystal axis,  $H \parallel [101]$  and  $H \perp [101]$  axis. In figures 1a and 1b we present dc  $\chi$  as a function of  $T$  below 25 K ( $H_{dc} = 10$  Oe) for the zero-field



**Figure 2.** Magnetic relaxation behavior ( $M$  vs.  $\log t$ ) of  $Sr_3CuIrO_6$ ; (a) and (b) for polycrystals and (c) for single crystals at low temperatures.

cooled (zfc) states of the specimens measured on an Oxford Instruments vibrating sample magnetometer (VSM).

### 3. Results and discussion

Figures 1c and 1d show ac  $\chi$  in the same  $T$  range at a frequency of 1 Hz ( $H_{ac} = 1$  Oe) measured on a quantum design SQUID magnetometer. Magnetic relaxation at 2.5 K and 12 K, measured using the VSM, is shown in figure 2. From the magnitudes of low-field (zfc) dc as well as ac  $\chi(T)$  (figure 1) for the two crystal orientations stated above, we infer that the easy axis of magnetization lies normal to the [101] direction. For comparison, in figures 1a and 1c we display the corresponding dc and ac  $\chi(T)$  behavior respectively, of the polycrystalline form reported earlier [1,2]. We find that the prominent feature due to magnetic ordering below 19 K in the polycrystalline form is extremely weak in the single crystals. In contrast, the minor shoulder around 5 K in dc  $\chi$  (absent in ac  $\chi$ ) in the polycrystalline data, becomes prominent in the single crystals in the form of a large upturn indicating bulk ordering. The intensity is at least an order of magnitude greater (dc  $\chi$ ) than that at the 19 K transition. Thus, this material is found to be characterized by at least two magnetic transitions, at about 5 K ( $T_1$ ) and 19 K ( $T_2$ ), with contrasting relative magnitudes in the single crystal versus the polycrystalline form.

We believe that an explanation in terms of two separate magnetic transitions for Cu and Ir at  $T_1$  and  $T_2$  cannot account for the very different magnitudes of  $\chi$  response at these transitions. If it were so, one would expect comparable extents of anomaly in  $\chi$  at  $T_1$  and  $T_2$  since both Cu and Ir here have spin = 1/2. Our argument which follows, is however independent of this interpretation. We also rule out spin-reorientation effects as a possible

cause of these transitions, considering that the intensity at  $T_2$  is weak and the behavior is sample dependent (also see ref. [1]). We instead attribute this to the formation of magnetic segments separated by random defects along the Cu–Ir chains. The contrasting single versus polycrystalline  $\chi(T_1)$  and  $\chi(T_2)$  response is also possibly related to the shortened chain lengths in the randomly oriented microcrystallites which form the polycrystals, as compared to those in the single crystals. Further work is required to understand the full implications of these findings.

A careful look at the dc as well as ac  $\chi$  data reveals that the behavior below 5 K is in fact a superposition of features due to at least two transitions separated by about 1 K, marked by vertical arrows in figure 1. The relative contributions to  $\chi$  appear to be a sensitive function of  $H$ , as revealed by the reversal of the peak positions in the dc and ac  $\chi$  plots. It is interesting that we observe multiple magnetic transitions (as a function of temperature/field) in a chemically homogeneous material.

There are major differences even in the magnetic relaxation behavior at 2.5 K and 12 K, and between the single and polycrystalline samples. The following sequence of measurements was adopted: The samples were zero field cooled to the desired temperature. A magnetic field of 5 kOe was then applied and switched off after 5 min. After the field had become zero, the magnetization ( $M$ ) vs. time ( $t$ ) data were collected for about 2 h. The  $M(\log t)$  data are shown in figure 2. In the case of polycrystals,  $M$  at 2.5 K decreases as  $\log t$  in consistence with the spin-glass-like behavior reported earlier [1]. We find that this behavior persists till about 5 K. However, at 12 K, after the initial drop,  $M$  surprisingly increases with  $t$  against the expected behavior. In the case of the single crystals for  $H \perp [101]$ ,  $M$  at 2.5 K actually attains negative values immediately after  $H$  is switched off. The values however become less negative with time. The full implications are however, not clear at present. We believe that the negative  $M$  is not due to any remanent negative field, as the data taken in the presence of a small positive field ( $zfc/fc$ ) also show an initially negative  $M$  followed by slow relaxation to positive values. If the absence of negative remanent field is confirmed, then this is a novel finding. Finally, we do not notice any magnetic relaxation beyond 5 K in the single crystal, and not at all for  $H \parallel [101]$  (down to 2 K) due to the weakness of the signal in that orientation.

#### 4. Conclusion

To conclude, we have observed that the ac and dc magnetic susceptibility behavior of the single crystalline spin-chain compound  $\text{Sr}_3\text{CuIrO}_6$  is distinctly different from its polycrystalline form. We also find unusual magnetic relaxation behavior, the implications of which need to be understood further.

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*Growth of a single crystal of Sr<sub>3</sub>CuIrO<sub>6</sub>*

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