Magnetic and superconducting properties of single crystals of $Sr_2HoRu_{1-x}Cu_xO_6$ grown from high temperature solutions

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Single crystals of $Sr_2HoRu_{1-x}Cu_xO_6$ (with $x=0-0.2$), measuring 2–3 mm across have been grown from $PbO-PbF_2$ based solutions in the temperature range of 1250–1150 °C. The crystals exhibit octahedral morphology and belong to the monoclinic space group $P2_1/n$. While Sr_2HoRuO_6 is found to be antiferromagnetic with weak ferromagnetism below 30 K, the solid solutions containing Cu exhibit a diamagnetic transition at 31 K which increases in magnitude and temperature with increasing Cu. Through a correlation of magnetic and calorimetric properties, these crystals are concluded to be spin-glass superconductors. © *2006 American Institute of Physics*.
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Sr_2HoRuO_6 belongs to a new family of double perovskites being investigated for their interesting magnetic and superconducting properties[1–7]. Doi *et al.*[4,5] showed that it is antiferromagnetic at low temperatures (<30 K) crystallizing in the monoclinic $P2_1/n$ space group. Wu *et al.*[7] reported a superconducting transition at 30 K in $Sr_2HoRu_{0.9}Cu_{0.1}O_6$. Recently we have grown single crystals of the solid solutions, such as $Ba_2YRu_{1-x}Cu_xO_6$,[8] $Sr_2YRu_{1-x}Cu_xO_6$,[9] $Ba_2PrRu_{1-x}Cu_xO_6$,[10] and $Ba_2HoRu_{1-x}Cu_xO_6$,[11] and reported their crystal structure and magnetic properties which are in agreement with the findings of Wu *et al.*[6,7] $Ba_2HoRu_{1-x}Cu_xO_6$ is the only nonsuperconducting material of these series. In this letter we report the magnetic and superconducting properties of the single crystals of $Sr_2HoRu_{1-x}Cu_xO_6$ (hence forth referred to as SrHo2116 for brevity) solid solutions with $x=0-0.2$.

SrHo2116 was prepared by thoroughly grinding an appropriate mixture of $SrCO_3$, Ho_2O_3, Ru, and CuO powders and sintering it in the temperature range of 900–1100 °C until their powder x-ray diffraction (XRD) patterns showed no further change. In a typical crystal growth run, 1 g of SrHo2116 powder was mixed with the flux mixture (consisting of 3 g of PbO, 1 g of PbF_2, 1 g of KF, and 0.01 g of B_2O_3), packed into a platinum crucible and covered tight with a platinum lid. Details of the crystal growth by cooling the solutions slowly from 1250 to 1150 °C in a silicon carbide heating element furnace have been described elsewhere.[9]

The microstructure of the grown crystals was investigated by XRD and electron microscopy combined with energy dispersive spectroscopy (EDS). The magnetic properties were measured using a superconducting quantum interference device magnetometer. Calorimetric properties were measured using a homemade microcalorimeter.

Figure 1 shows the optical micrograph of the crystals that nucleated and grew on the surface of the solution as well as at the bottom of the crucible. The former measure 2–3 mm across and 0.5 mm thick with nearly flat faces on top (top right corner) and broken surfaces (due to hopper growth) at the bottom (lower right corner). The latter are smaller (~0.5–1.0 mm) but well separated from each other and the flux. All crystals show identical characteristics and exhibit an octahedral habit.

The powder XRD patterns of SrHo2116, $x=0$ and $x=0.1$ crystals are shown in Fig. 2(a). They were analyzed

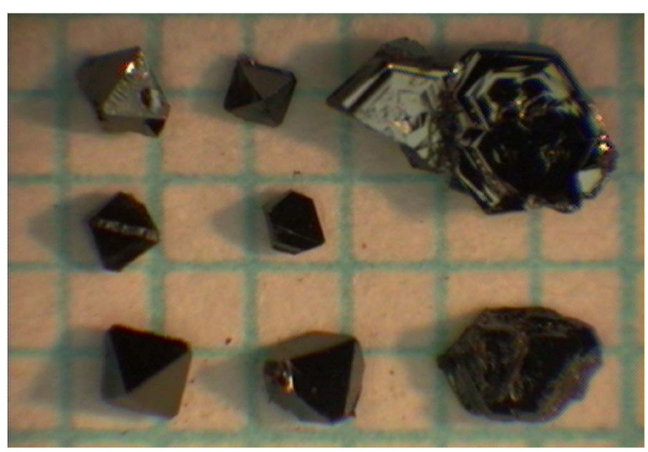

FIG. 1. Optical micrograph of SrHo2116 crystals grown at 1200 °C.

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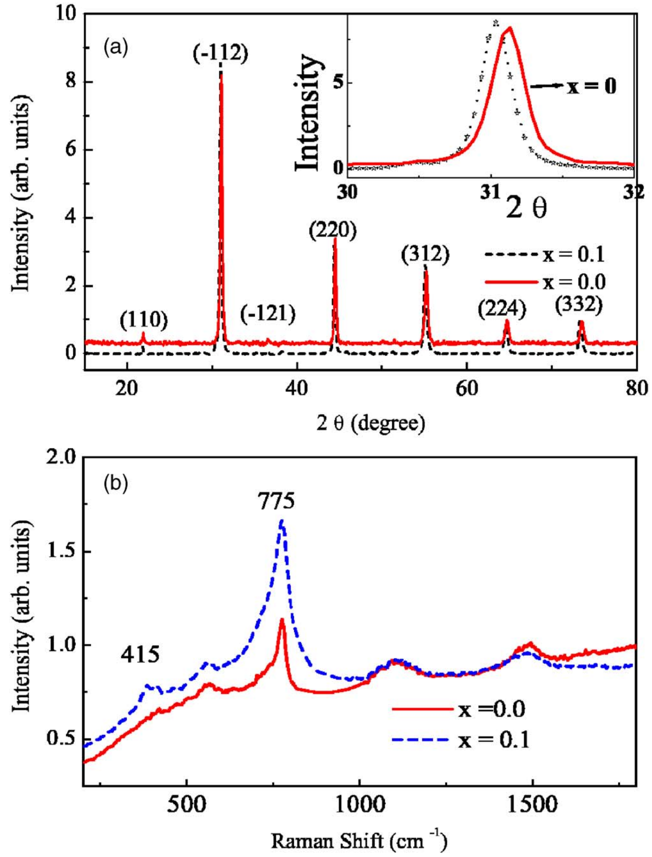

FIG. 2. (a) XRD patterns of the SrHo2116 crystals at $x=0$ (solid line) and $x=0.1$ (dashed line) and (b) Raman spectra of $x=0.0$ (solid line) and $x=0.1$ (dashed line) crystals.

using the XPERT PLUS program (Phillips). The $x=0$ pattern fits to the monoclinic space group $P2_1/n$ with lattice parameters $a=5.753(3)$ Å, $b=5.755(3)$ Å, $c=8.090(8$ Å), and $\beta=90.01(8)°$ and the volume of the unit cell $V=267.848\times10^6$ pm^3, which are very close to those reported by Doi *et al.*[5] The patterns do not show any unidentified peaks indicating a pure phase of SrY2116. For the Cu doped crystal with $x=0.1$, the peaks are found to shift to a lower 2θ value (only the 31° peak given in the inset for clarity), indicating that the incorporation of Cu leads to larger lattice parameters. The EDS analysis (not presented here) shows the presence of 0.35–0.45 at. % of Cu in these crystals which is nearly 40% of the 1 at. % added. The Raman spectra of these crystals shown in Fig. 2(b) display a slight shift to lower frequencies (relative to $x=0$), indicating an increase in the bond lengths of the RuO_6 octahedra in the presence of Cu, in good agreement with XRD results.

Temperature (T) dependence of the molar magnetic susceptibility (χ) of the SrHo2116, $x=0$ crystals for 10 Oe and 1 kOe field (H) is shown in Figs. 3(a) and 3(b), respectively. The 10 Oe zero field cooled (ZFC) curve shows two peaks at 20 and 29 K while the field cooled (FC) curve shows a single peak at 20 K. The ZFC and FC curves show a divergence below 35 K. These curves appear similar to those reported by Doi *et al.*[5] with $H=1$ kOe in all the Raman-active peaksin all the Raman-active peaks.

The 1 kOe ZFC curve shown in Fig. 3(b) exhibits two peaks at 14.5 and 20 K, while the 1 kOe FC curve decreases monotonically as the temperature is increased. These two curves also diverge at 35 K. The inset of Fig. 3(b) displays the variation of T vs $(\chi_M)^{-1}$ for the 1 kOe curves. A fitting of the paramagnetic region above 150 K to the Curie-Weiss law yields an effective magnetic moment of $10.75\mu_B$ and a Curie-Weiss constant θp of −19.85 K. The negative θp indicates a predominantly antiferromagnetic interaction in the crystals, which agrees with the reported results.[5]

The M-H curves recorded at 5 K with ZFC (circles) and 200 Oe FC (squares) conditions, shown in Fig. 3(c), are identical and exhibit a small hysteresis indicating a single phase ordered crystal exhibiting weak ferromagnetism.[5] Thus all the properties of the SrHo2116, $x=0$ crystals are identical to the reported polycrystalline samples.[5]

The temperature dependence of χ of SrY2116, $x=0.1$ crystals are presented for $H=10$ Oe and 1 kOe in Figs. 4(a) and 4(b), respectively. The 10 Oe ZFC curve exhibits a diamagnetic transition at 31 K, indicative of superconductivity. The magnitude and temperature of this transition are found to increase with increasing Cu [inset Fig. 4(a) where circles represent crystals with $x=0.1$ and the stars $x=0.2$]. A peak appears in the paramagnetic region of the ZFC curve whose magnitude increases and temperature decreases as H is increased. As seen in Fig. 4(b), the peak is observed at 25 K and an upturn below 15 K, in the 1 kOe ZFC curve, which is different from the $x=0$ crystals. The diamagnetic response below 31 K, which was also observed by Wu *et al.*,[7] may be a result of freezing of the fluctuating spins of Ru as observed by Harshman *et al.*[12] The appearance of a peak at 25 K in the 1 kOe ZFC curve [Fig. 4(b)] indicates the spin-glass nature[12] of the above transition. The presence of a broad hump rather than a peak around the transition temperature of 31 K in the specific heat data shown in the inset of Fig. 4(b) strongly supports this conclusion. Unlike $Sr_2YRu_{0.9}Cu_{0.1}O_6$,[12] we do

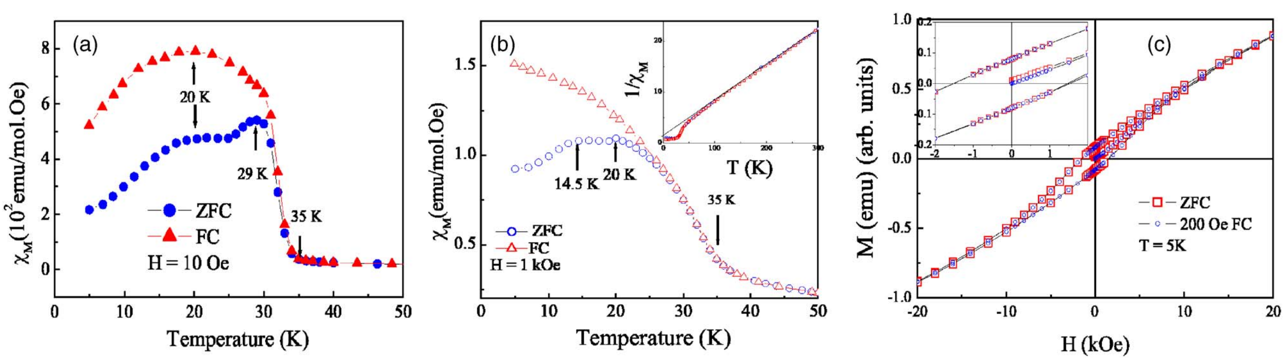

FIG. 3. Temperature variation of χ_M for the SrHo2116, $x=0$ crystals for (a) $H=10$ Oe and (b) 1 kOe (inset χ_M^{-1} vs T). (c) $M-H$ curves recorded at 5 K in ZFC and 200 Oe FC condition; inset gives an enlargement of the low field region.

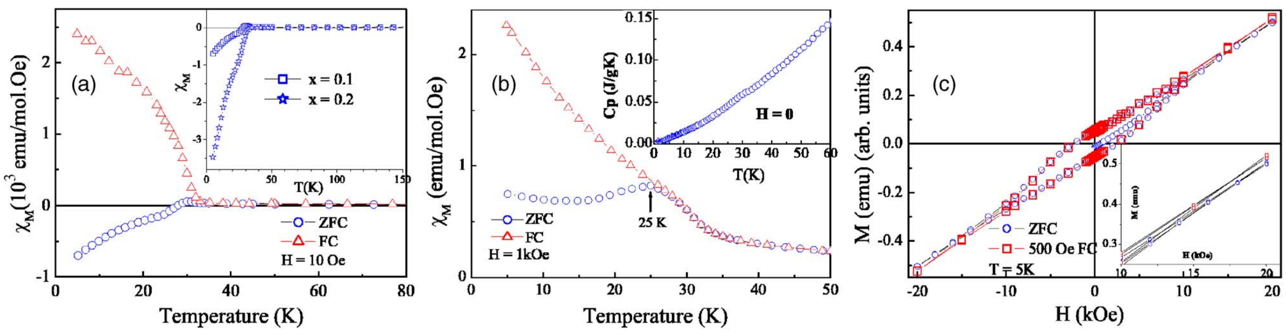

FIG. 4. Temperature variation of χ_M for the SrHo2116, $x=0.1$ crystals recorded at $H=10$ Oe (a) and $H=1$ kOe (b), inset giving the Cp vs T variation at $H=0$. (c) ZFC (circle) and 500 Oe FC (squares) $M-H$ curves of $x=0.2$ crystal recorded at 5 K; inset gives an enlargement of a section in high field region.

not observe a peak at 23 K in our crystals (in the 10 Oe ZFC curve), indicative of the ordering of Ru moments. Instead a broad anomaly is seen at 25 K in the 10 Oe field ZFC curve [Fig. 4(a)] which may indicate the beginning of ordering. Ordering of both the Ru and Ho moments was reported[7] at 23 and 15 K, respectively, giving a zero resistance at 15 K in the $Sr_2HoRu_{0.9}Cu_{0.1}O_6$ bulk samples annealed in an atmosphere of 1:9 mixture of Ar and O_2. In the absence of Ho and Ru ordering, the spin fluctuations continue with cooling as observed in our samples. It is likely that the Cu concentration is insufficient (as discussed later) to bring about the ordering of the Ru and Ho spins in the SrHo2116 crystals that is needed to observe superconductivity.[12] The FC curves decrease monotonically as the temperature is increased in all these samples.

The ZFC (circles) and 500 Oe FC (squares) M-H curves recorded at 5 K on $x=0.2$ crystals are depicted in Fig. 4(c). The hysteresis loop is broader and the moment increases linearly with field, unlike the nonlinear variation in the case of $x=0$. These curves do not appear to represent either a weak ferromagnetic (of the parent compound) or a superconductor. Further, the FC hysteresis loop appears to shift in an anticlockwise direction as H is increased; the increase in the moment being more at the extremes than the center [inset of Fig. 4(c)]. Such increase in moment of the FC magnetization is a further confirmation of the spin-glass behavior.[5,10,13,14]

The EDS, XRD, and Raman spectra confirm the presence of Cu in the crystals, but much less than the amount added, probably due to the evaporation loss.[9,10] In addition, conversion of CuO to Cu_2O above 1200 °C (Refs. 9 and 15) may incorporate Cu, both as Cu^{+} and Cu^{2+} at the crystal growing temperatures. A Cu-valence higher than 2+ is needed to observe the superconductivity in this system as proposed by Ren and Wu.[16] It is therefore likely that the present crystals comprise dilute solid solutions of Cu of mixed valence states behaving more like spin-glass superconductors[10,15] rather than a regular superconductor. Supporting investigations such as specific heat [inset Fig. 4(b)], magnetic moment, and hysteresis measurements in different transition temperature ranges and transition temperatures (not presented here for want of space) made as in the case of $B_2PRu_{1-x}Cu_xO_6$ system[10,14] also confirm this conclusion. We have not observed a resistive transition in these samples for reasons discussed above and probably due to lack of connectivity. It is generally believed that single crystals require much longer duration of atmosphere annealing than the bulk as in the case of $YBa_2Cu_3O_{6+\delta}$.[10] Since bulk samples[7] were annealed in a 1:9 mixture of Ar and O_2 at 1410 °C, these crystals may also require a similar treatment. It may also be necessary to grow the crystals in a positive pressure of O_2 to prevent the conversion of CuO to Cu_2O. Efforts are being made in this direction.

In conclusion, single crystals of SrHo2116, $x=0-0.2$, grown from $PbO-PbF_2$ based solutions exhibit a weak ferromagnetism with $x=0$ and superconductivity at 31 K in the presence of Cu.

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