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Abstract. The structure of $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ has been analysed using the Rietveld technique. The electrical resistivity, Hall constant, thermoelectric power and specific heat of the sample are measured as functions of temperature. $T_c^{R=0}$ for the sample is 51 K and remains unchanged under annealing in a hydrogen + argon atmosphere. The Hall angle $\cot\theta_H$ shows a T^2 dependence with temperature. The thermoelectric power is found to be positive and large and follows a dome-shaped curve with T. The specific-heat anomaly associated with the superconducting transition is broad and small. From the low-temperature specific-heat result the Debye temperature θ_D has been estimated to be 234 K.

1. Introduction

Superconductivity in $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ with $m = 1$, 2 and 3 has been reported by different groups [1–3] with T_c-values of 94 K, 123 K and 133 K, respectively. Substitution studies at the Ba site by Sr/La and at the Hg site by Cr/Bi/Mo on $HgBa_2CuO_{4+\delta}$ (Hg-1201) were reported by Shimoyama *et al* [4], Pelloquin *et al* [5] and Singh *et al* [6]. The T_c-values of the substituted samples are less than that for pure $HgBa_2CuO_{4+\delta}$, for instance 58 K for Cr-substituted [4], 27 K for Bi-substituted [5] and 78 K for Mo-substituted samples [6]. Strontium-based mercury samples are quite stable under ambient air, and so it is possible to study different properties over a long period of time. We have prepared $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ (nominal composition) and measured the structural properties, electrical resistivity, Hall effect, thermoelectric power (TEP) and specific heat as functions of temperature. The effect of annealing under a hydrogen+argon (H+Ar) atmosphere with temperature is also studied. From the electrical resistivity ρ and Hall constant R_H we have estimated the Hall angle $\cot\theta_H$ and its dependence on temperature. The TEP and specific-heat data are analysed on the basis of existing knowledge, and the Debye temperature Θ_D has been estimated from the low-temperature (4.2–10 K) specific-heat result.

2. Experimental details

The samples were synthesized following the solid state reaction between the precursor, and HgO. To synthesize the precursor, stoichiometric amounts of $Sr(NO_3)_2$ and $Cu(NO_3)_2.3H_2O$ were dissolved in water. The solution was dried to a blue powder and then heated slowly in

an alumina crucible until the NO_2 gas was completely driven out. Stoichiometric amounts of Cr_2O_3 were then mixed with it and fired at 900 °C for 24 h. A black precursor powder was obtained and immediately put in a dry box, where the HgO powder and the precursor were mixed together. Finally, the mixture was pressed into pellets. Each pellet (13 mm in diameter and about 1.5 mm thick) was divided into two pieces, introduced into a quartz tube, evacuated and sealed. The pellets were sintered at 880 °C for 8 h and finally quenched to room temperature. A black product was obtained together with a drop of mercury inside the tube.

The as-prepared samples were annealed at 300 °C in an oxygen atmosphere for 1 h and cooled slowly to room temperature. The samples were characterized using a Philips x-ray diffractometer with Cu Kα radiation. The powder x-ray diffraction (XRD) patterns for all the samples are the same and one representative spectrum is shown in figure 1. The samples are primarily of single phase having a Hg-1201 structure. A few impurity lines of $SrCuO_2$ appeared in the x-ray pattern with a very low intensity. To estimate the amount of $SrCuO_2$ in our sample we made a quantitative phase analysis using a Rietveld refinement program (DBWS-9411). X-ray data were collected in the 2θ range 15–100° with 0.03° step width and counting time 6 s/step.

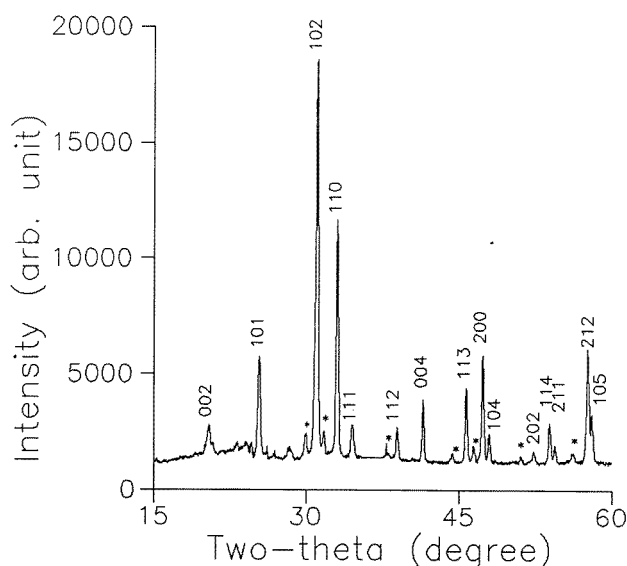**Figure 1.** Powder XRD pattern of $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$: *, peak for the impurity phase $SrCuO_2$.

To change the oxygen content of the samples we have annealed them further in a H+Ar (1:4) atmosphere for 2–6 h. X-ray studies were performed on these samples also and we found that, for an annealing temperature greater than 350 °C, the samples decompose.

The resistances of the samples were measured by the four-probe technique. For Hall measurements we have used five terminals (two for current and three for voltage). For high-temperature resistivity measurement, platinum wires were used for lead connections and a platinum resistance thermometer for measuring the sample temperature. The specific heat of the sample was measured with an automated adiabatic heat calorimeter in which a calibrated germanium resistance was used as the temperature sensor. The apparatus used for measuring the TEP of the samples was described earlier [7].

3. Results and discussion

At the first stage of the Rietveld analysis the structure of Hg$_{0.7}$Cr$_{0.3}$Sr$_2$CuO$_{4+\delta}$ ((Hg, Cr)-1201) was refined using the tetragonal symmetry of space group $P4/mmm$. The initial values for the lattice parameters were obtained from a least–squares fit of the powder diffraction peaks and those for the other structural parameters were taken from a report of a neutron diffraction study on (Hg, Cr)-1201 sample [8]. In the second stage of refinement the impurity phase SrCuO$_2$ was included. The starting values for the structural parameters for this phase were taken from [9]. The observed and calculated patterns are shown in figure 2. To determine the oxygen position in the (Hg, Cr)–O layer, in our refinement we tried four different models. In the first model A, we considered O(3) atoms to be fixed at $(0.5, 0.5, 0)$. After refinement the Hg, Cr and O(3) occupancies were found to be 61%, 39% and 66%, respectively. On the other hand, when we tried displacements $(0.5 - d', 0.5 - d', 0)$ for O(3) in the second model B, we got Hg and Cr occupancies of 58% and 42%, respectively. Due to the fourfold position of the O(3) atom the total oxygen content in the (Hg, Cr)–O plane becomes 76%. As was done by Chmaissem *et al* [10], we also tried refinements introducing new oxygen atoms O(4) at the $(0.5, 0, 0)$ position in the third model C while, in the fourth model D, both O(3) and O(4) atoms were introduced. The R-factors for all the four models are given in table 1. Since the R-factors for four different models do not differ appreciably, we are not able to make any definite conclusion about which model is suitable for our sample (Hg, Cr)-1201. However, in our neutron structure refinement studies [8] on the same sample, no occupancy of Cu at the (Hg, Cr) site was detected. Since the occupancy at O(4) site is linked to a definite occupancy of Cu at the Hg site, we may ignore model C and model D in our case. Now the total oxygen content in the (Hg, Cr)–O layer in model A is 66% while the value in model B is 76%. This latter value (76%) is very much closer to the corresponding value (80%) determined from our neutron diffraction study [8]. In addition the occupancies (58% and 42%) for Hg and Cr as obtained in model B also agree well with those reported in [8]. So we may conclude that the results of our model B may be best fitted with the neutron diffraction results of (Hg, Cr)-1201. For illustration the refined parameters and interatomic bond distances according to model B are listed in tables 2 and 3, respectively. Refined parameters a and c are 3.8419 Å and 8.7245 Å, respectively (table 2), which are in good agreement with those reported by Shimoyama *et al* [4] and Chmaissem *et al* [10]. The c-axis length is considerably shorter than that for Hg-1201 (9.51 Å) whereas a differs by only about 0.02 Å. We have estimated the oxygen content per unit to be 4.38. Using refined scale factors for the two phases the weight percentage of SrCuO$_2$ has been estimated to be 10%.

Table 1. *R*-factors for the four different models.

Model	R_p (%)	R_{wp} (%)
A with O(3) at $(0.5, 0.5, 0)$	6.52	8.74
B with O(3) at $(0.5 - d', 0.5 - d', 0)$	6.42	8.59
C with O(4) at $(0.5, 0, 0)$	6.66	8.89
D with O(3) and O(4)	6.47	8.61

The temperature dependence of resistivity for (Hg, Cr)-1201 (annealed at 300 °C in an oxygen atmosphere for 1 h) is shown in figure 3. In the same figure we plot the resistance for the sample annealed at 350 °C in a H + Ar atmosphere for 6 h. The $T_c^{R=0}$-values for the
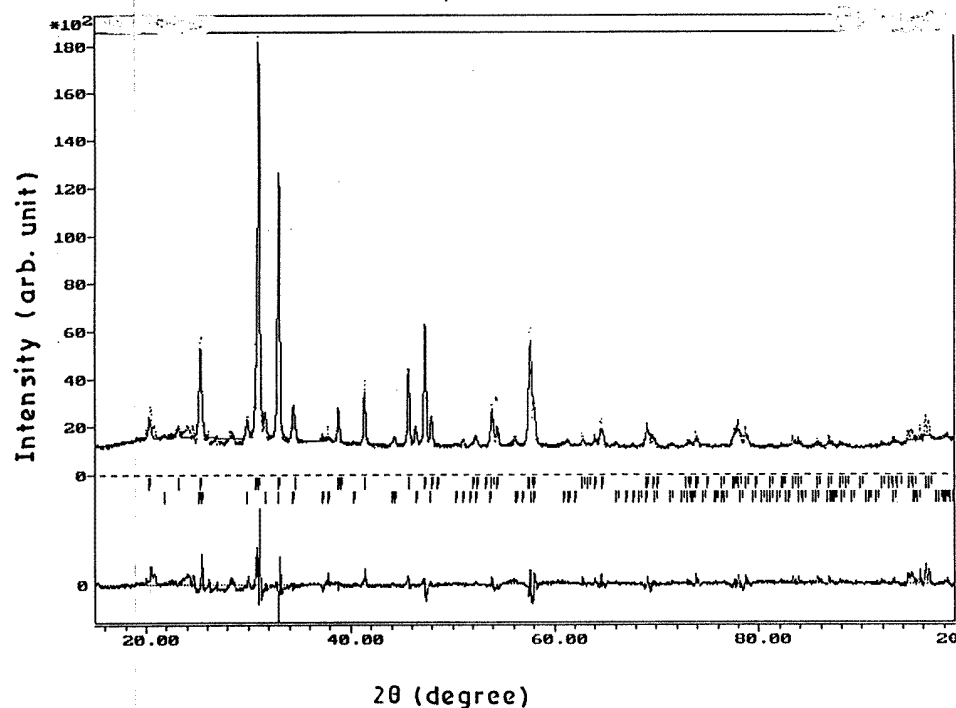
Figure 2. The observed ($\cdots\cdots$), calculated (——) and difference powder XRD profiles of $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ and $SrCuO_2$. The short vertical lines represent the Bragg reflection positions for $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ (top) and $SrCuO_2$ (bottom).

Table 2. Refined structural parameters for $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ (symmetry, tetragonal; space group, $P4/mmm$; cell parameters $a = 3.842(2)$ Å and $c = 8.724(4)$ Å; $R_p = 6.42\%$; $R_{wp} = 8.59\%$; $R_{exp} = 2.53\%$).

Atom	Site	x	y	z	B (Å^2)	n
Hg	1a	0	0	0	2.81(11)	0.58(1)
Cr	1a	0	0	0	2.81(11)	0.42(1)
Sr	2h	0.5	0.5	0.3009(4)	0.77(10)	0.91(1)
Cu	1b	0	0	0.5	1.08(19)	1.02(2)
O(1)	2e	0	0.5	0.5	2.0	0.97(4)
O(2)	2g	0	0	0.2008(30)	2.0	0.84(3)
O(3)	1c	0.3590(10)	0.3590(10)	0	2.0	0.19(2)

samples annealed in oxygen and in a H + Ar atmosphere are the same (51 K), indicating no charge in T_c with oxygen content.

In the oxygen-annealed sample, ρ varies linearly with temperature in the range 62–215 K. Above this temperature the resistivity curve deviates from linearity and shows a saturation trend. This behaviour persists up to 450 K, the maximum temperature that we studied. The (H + Ar)-annealed sample also shows similar saturation. Harris *et al* [11] and Meng *et al* [12] observed a similar resistivity behaviour for $HgBa_2CaCu_2O_{6+\delta}$ and attributed it to the insulating phase formed at the grain boundaries or to the loss of mercury

Table 3. Interatomic distances.

Bond	Distance (Å)
Hg–O(2) × 2	1.751
Hg–O(3) × 4	1.929
Sr–O(1) × 4	2.590
Sr–O(2) × 4	2.854
Sr–O(3) × 4	2.741
Cu–O(1) × 4	1.921
Cu–O(2) × 2	2.611
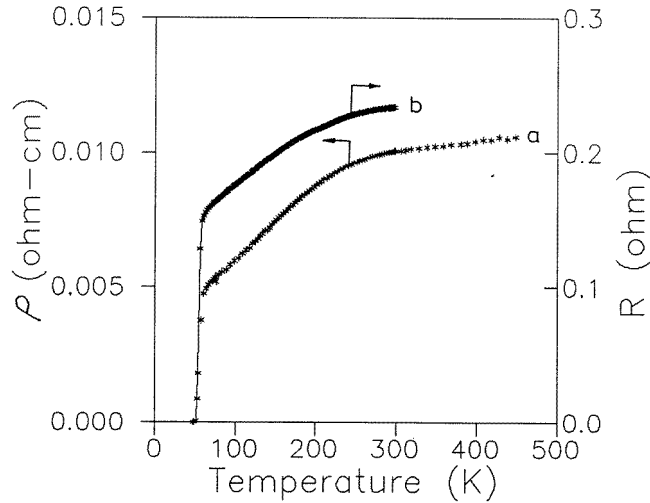
Figure 3. (*a*) Resistivity as a function of temperature for Hg$_{0.7}$Cr$_{0.3}$Sr$_2$CuO$_{4+\delta}$ annealed at 300 °C in oxygen for 1 h. (*b*) Resistance for the same sample annealed at 350 °C in H + Ar for 6 h.

due to long-time annealing. However, similar variation was found for our (Hg, Cr)-1201 sample annealed at 300 °C for 1 h, suggesting only that the downward trend is not due to the loss of mercury. We have prepared the material four times and all the samples show resistivity saturation although it is difficult to believe that this could be an intrinsic property of the sample. Moreover, such saturation has not been observed in other high-T_c materials. Recently prepared (Hg, V)Sr$_{2-x}$La$_x$CuO$_{4+\delta}$ samples [13] also do not show any saturation in resistivity. Hence, further investigation is essential to understand the resistivity saturation in the (Hg, Cr)-1201 system.

A rise in T_c with decrease in spacing between Cu–O planes is considered to be an important feature for high-T_c materials. Harshman and Mills [14] showed that phase pure layered compounds exhibit a relation of the form

$$k_B T_c \propto (\epsilon d)^{-1} \tag{1}$$

where ϵ is the average dielectric constant and d is the interplaner spacing. Kawabata and Nakanishi [15] obtained a linear relationship between T_c and the spacing d between Cu–O (or other elements) sheets along the c axis of a perovskite structure as

$$T_c = -158.02d + 611.40. \tag{2}$$

To check whether this relation (equation (2)) is also obeyed by the Hg system we consider two Hg samples, namely $HgBa_2CuO_{4.15}$ and (Hg, Cr)-1201 which have the same carrier concentration ($p \simeq 0.10$). The parameter c for the former sample is 9.53 Å [16] and that for the latter is 8.7 Å. From the structural data the d-spacings between BaO–CuO_2–BaO and SrO–CuO_2–SrO for these two samples are 3.84 Å and 3.47 Å, respectively. Corresponding T_c-values calculated from equation (2) are 4 K and 63 K whereas the measured values are 80 K [16] and 51 K. Thus the T_c–d conjecture does not seem to be valid for the Hg system. A similar observation was reported from a pressure experiment on $Y_2Ba_4Cu_7O_{15.32}$ [17] and Tl-2223 [18] systems.
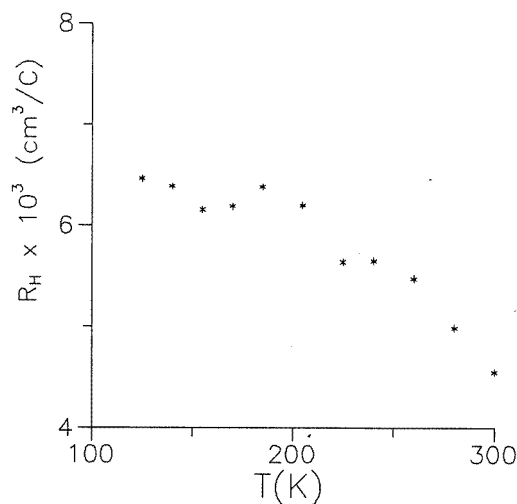

Figure 4. Variation in Hall constant with temperature for $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$.

The Hall constant R_H for the sample is positive and its variation with temperature is shown in figure 4. To explain the transport properties of high-T_c systems, Anderson [19] proposed two different relaxation rates: the transport relaxation rate ($\tau_{tr} \propto T^{-1}$) and the Hall relaxation rate ($\tau_H \propto T^{-2}$). It was predicted that in this model the Hall angle should follow the relationship

$$\cot\theta_H = \alpha T^2 + \beta. \tag{3}$$

To check the validity of the relation in our sample we fitted our experimental points and found that the mean square deviation is minimum for T^2-dependence. The plot of $\cot\theta_H$ with T^2 is shown in figure 5. The parameters α and β obtained for our sample are 0.0745 and 415, respectively. Harris *et al* [11] measured the temperature dependence of the Hall constant for two $HgBa_2CaCu_2O_{6+\delta}$ polycrystalline samples (samples A and B) and analysed them on the basis of the Anderson model. α- and β-values obtained for their samples are 0.186 and 2020 for sample A, and 0.0891 and 337 for sample B. It is known that β tends to zero when the impurity content in the samples is negligible [11]. The ratio β/α is, therefore, a measure of the purity of the material and this ratio for our sample is 5570. One may compare this value with those (10 860 for sample A and 3780 for sample B) for the samples of Harris *et al*. A smaller ratio indicates that the doping to the Hg layers in the sample introduces less disorder for electronic transport in the Cu–O planes.
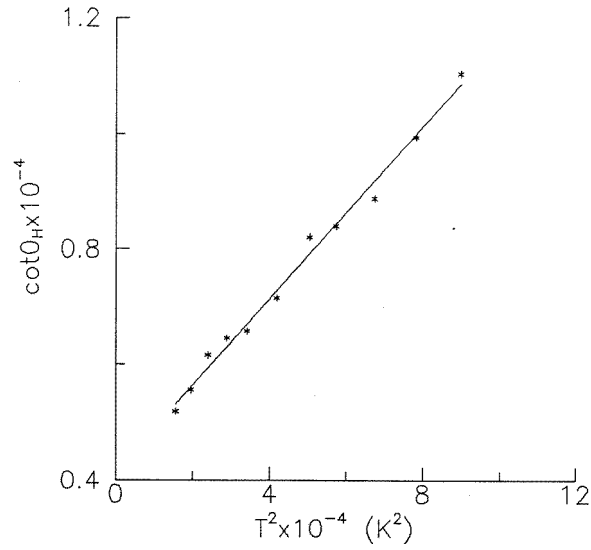
Figure 5. Plot of $\cot\theta_H$ versus T^2 for Hg$_{0.7}$Cr$_{0.3}$Sr$_2$CuO$_{4+\delta}$: ——, best-fit curve to the relation $\cot\theta_H = \alpha T^2 + \beta$.

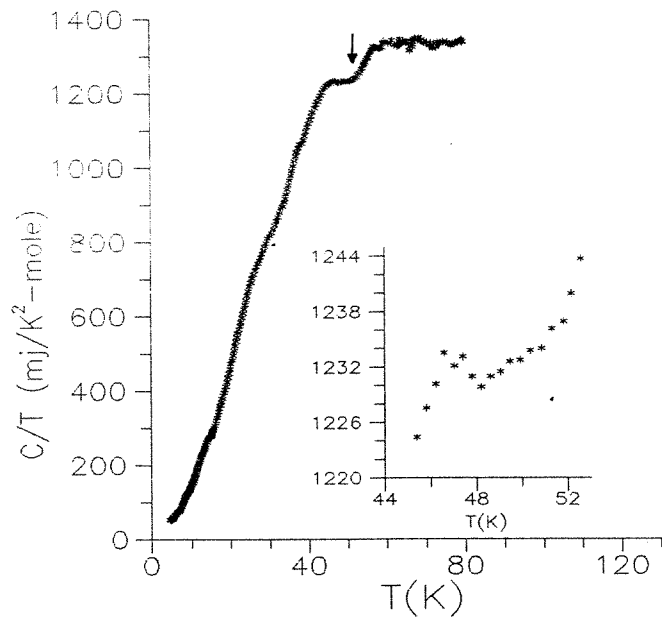**Figure 6.** Plot of C/T against temperature for the Hg$_{0.7}$Cr$_{0.3}$Sr$_2$CuO$_{4+\delta}$ sample. The inset shows data near the transition on an enlarged scale.

In figure 6 the specific-heat data for Hg$_{0.7}$Cr$_{0.3}$Sr$_2$CuO$_{4+\delta}$ are shown as C/T versus T in the temperature range 4.2–80 K ($T_c^{R=0}$ obtained from the resistance measurement is indicated by an arrow). The specific-heat values for the sample are of the same order as

those reported by Woodfield *et al* [20] for $HgBa_2CuO_{4+\delta}$. The low-temperature specific-heat data (4.2–10 K) are fitted with the equation

$$C = \gamma T + \beta_3 T^3 + \beta_5 T^5 \tag{4}$$

and the best-fit parameters are $\gamma = 24.847$ mJ mol^{-1} K^{-2}, $\beta_3 = 1.1898$ mJ mol^{-1} K^{-4} and $\beta_5 = 4.2656 \times 10^{-4}$ mJ mol^{-1} K^{-6}. From β_3 we have estimated that $\Theta_D = 234$ K, and this is comparable to $\Theta_D = 217$ K reported by Woodfield *et al* [20] for the $HgBa_2CuO_{4+\delta}$ system. Such a low value for Θ_D suggests a relatively soft lattice. The specific-heat anomaly associated with the superconducting transition in (Hg, Cr)-1201 is comparatively broad and small. A possible reason is the inhomogeneity and/or impurities present in the sample. However, non-availability of the data above 80 K prevents us from estimating $\Delta C/T_c$ in this system.
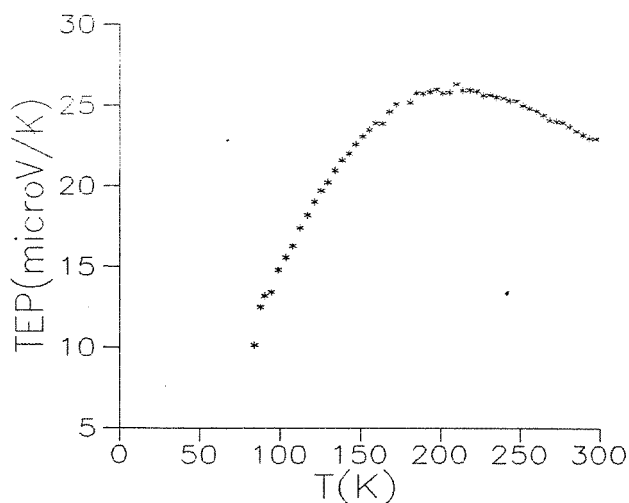

Figure 7. The TEP as a function of temperature for the $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ sample.

The thermoelectric power S for the $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ sample is shown in figure 7 for the temperature range 77–300 K. S is 10 μV K^{-1} at 77 K; above this temperature it increases with increase in temperature, passes through a maximum (25 μV K^{-1}) at about 200 K and then decreases with further increase in temperature. The large positive TEP value indicates that the sample is in the underdoped region. The room-temperature TEP value is 23 μV K^{-1}. Obertelli *et al* [21] have shown a universal correspondence of the room-temperature TEP with p. Using the room-temperature S for our sample we found that $p \simeq 0.1$ per Cu ion. For $HgBa_2CuO_{4+\delta}$ the maximum T_c occurs at $p = 0.16$ per Cu ion. We failed to improve T_c for (Hg, Cr)-1201 by varying the Cr concentration and the annealing conditions.

4. Conclusion

We have measured the structural properties, electrical resistivity, Hall constant, TEP and specific heat of $Hg_{0.7}Cr_{0.3}Sr_2CuO_{4+\delta}$ (nominal composition). The $T_c^{R=0}$ of the system is 51 K. The Rietveld analysis of the XRD pattern suggests that the composition is $Hg_{0.58}Cr_{0.42}Sr_{1.82}Cu_{1.02}O_{4.38}$. From Hall data it is found that $\cot\theta_H$ is proportional to T^2.

The specific heat for (Hg, Cr)-1201 is more or less the same as that for Hg-1201, and the specific-heat anomaly associated with the superconducting transition is broad and small. The low-temperature (4.2–10 K) specific-heat result gives $\Theta_D \simeq 234$ K. The TEP is positive and large, suggesting that the system is in the underdoped region.

Acknowledgments

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