Superconducting and magnetic properties of $TlSr_2Ca_{1-x}R_xCu_2O_7$ [R=Pr, Tb]

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The magnetic and superconducting properties of the $TlSr_2Ca_{1-x}R_xCu_2O_7$ [R = Pr (x=0.2–1.0); Tb (x = 0.6 and 1.0)] system are reported. The observation of superconductivity in $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ (T_c = 74 K) suggests that the Pr ions are in the trivalent state. The value of the effective magnetic moment, μ_{eff} = 3.15 μ_B, for the $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ compound, lies between the free-ion values expected for Pr^{3+} ($3.58\mu_B$) and Pr^{4+} ($2.54\mu_B$). The reduced value of μ_{eff} for the Pr^{3+} ion is explained in terms of crystal-field effects. For $TlSr_2TbCu_2O_7$, the Tb magnetic moments order antiferromagnetically at 7.0 K, which is the highest magnetic ordering temperature among the known Tb-containing high-T_c related compounds. Superconductivity (T_c = 74 and 62 K) and antiferromagnetic ordering (T_N = 5 and 6.2 K) coexist in $TlSr_2Ca_{0.4}R_{0.6}Cu_2O_7$ with R = Pr and Tb, respectively.

I. INTRODUCTION

It has been well established that the substitution of Y in the $YBa_2Cu_3O_{7-\delta}$ compound by rare earths does not affect the superconducting properties, with the three exceptions Ce, Pr, and Tb. For Ce and Tb, it has not been possible to obtain a single-phase compound, while it has been observed that Pr can be easily substituted without affecting the orthorhombic structure, but it suppresses superconductivity.[1–3] The $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system has been extensively investigated to understand the depression of T_c with increasing x, shedding light on the basic mechanisms of oxide superconductivity.[4] Based on experimental and theoretical studies, two mechanisms have emerged. In one of the mechanisms, the values of the magnetic moment and the entropy associated with the magnetic ordering suggest that the Pr ions in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ are in a tetravalent or mixed-valent state, implying that the electron, removed from the Pr ion, is located in the CuO_2 plane, destroying the superconductivity. On the other hand, the spectroscopic measurements show that Pr is in the trivalent state and that superconductivity is depressed due to the overlap of the $4f$ orbitals with the O $2p$ – Cu $3d$ orbitals in the CuO_2 plane, leading to Abrikosov-Gorkov-type pair breaking and/or localization of holes in the CuO_2 planes. There are also mixed models, which assume that both hole filling and magnetic pair breaking are essential to explain the observed phenomenon.

Several of the rare-earth (R) ions in $RBa_2Cu_3O_{7-\delta}$ have been shown to exhibit long-range three-dimensional ordering for the f moments at low temperatures, coexisting with the superconductivity.[5,6] Coexistence of magnetic ordering and superconductivity suggests that the interaction of magnetic $4f$ electrons with the O $2p$–Cu $3d$ electrons are too weak to influence the superconducting properties of these compounds appreciably.

In view of the anomalous properties of Pr and Tb ions and in continuation of our study on superconductivity and magnetism in Tl-1:2:1:2 system, $TlSr_2Ca_{1-x}R_xCu_2O_7$, we report the results of the structural analysis, electrical resistivity, magnetic susceptibility, and theoretical analysis of the magnetic susceptibility data in terms of the crystalline electric field and exchange interaction for the same series with R = Pr and Tb.

II. EXPERIMENTAL

The systems $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ (x=0.0 – 1.0) and $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ (x=0.6 and 1.0) have been prepared by a method described elsewhere.[7] Phase purity of the materials was checked by the powder x-ray-diffraction method. Lattice parameters were obtained by a least-

squares-fitting procedure. dc electrical resistance measurements were carried out by a standard four-probe technique. Magnetic measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, USA) between 100 and 300 K for superconducting $TlSr_2Ca_{0.4}R_{0.6}Cu_2O_7$ (R=Pr,Tb) with an applied field of 20 kOe, and between 4.5 and 300 K for the semiconducting $TlSr_2TbCu_2O_7$ with an applied field of 3 kOe. We have also used an ac-susceptibility technique in which we employed a magnetic field of 2 Oe (rms) at a frequency of 21 Hz in the temperature range 1.5–30 K.

III. RESULTS AND DISCUSSION

X-ray powder diffraction patterns of the $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ system revealed that the material with $x = 0.6$ is single phase as shown in Fig. 1. Materials with other values of x contain small amounts of impurity phase(s). X-ray powder diffraction patterns of $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ ($x = 0.6$ and 1.0) showed that the materials are predominantly single phase with impurity phase(s) less than 7%. All the other lines can be indexed on the basis of a tetragonal 1:2:1:2 structure with space group $P4/mmm$. Lattice parameters for $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ are a=3.82 Å and c=12.11 Å; for $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ they are a=3.81 Å and c=12.04 Å for x=0.0 and a=3.82 Å and c=12.00 Å for x=1.0. The formula of the Tl-1:2:1:2 system can be written as $RA_2(TlCu_2)O_7$ (A=Ba, Sr), and its structure can be related to that of $RBa_2Cu_3O_7$ systems [replacing Cu-O chains in $RBa_2Cu_3O_7$ by a Tl-O plane in $RA_2(TlCu_2)O_7$]. However, unlike $RBa_2Cu_3O_7$ (except R=Ce, and Tb), the compounds $TlA_2RCu_2O_7$ (A=Ba, Sr) are semiconducting.

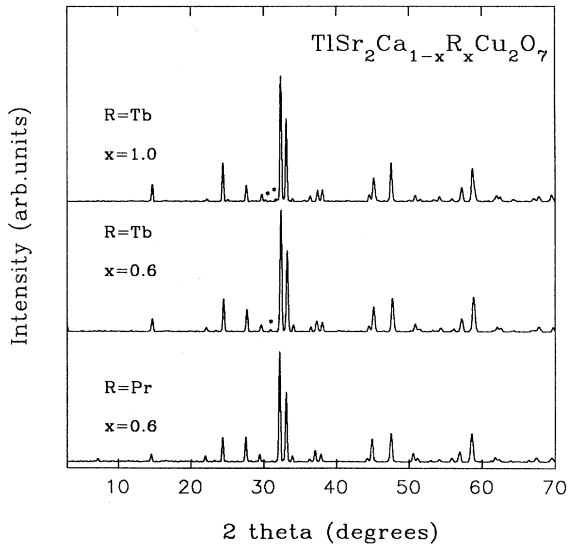

FIG. 1. Powder x-ray-diffraction patterns of $TlSr_2Ca_{1-x}R_xCu_2O_7$ [R=Pr (x=0.6); Tb (x=0.6 and 1.0)]. All the lines can be indexed on the basis of the tetragonal 1:2:1:2 phase with space group $P4/mmm$. In the case of the Tb samples, the lines marked (*) indicate the presence of a small amount (about 7%) of an impurity phase.

Normalized resistance versus temperature in the $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ system with x=0.2, 0.4, 0.6, and 0.8 is shown in Fig. 2. It is clear from this figure that except for the sample with x=1.0, all other samples are superconducting with T_c=58, 70, 74, and 38 K for x=0.2, 0.4, 0.6, and 0.8, respectively. T_c increases with the increase of x to a maximum of 74 K for x=0.6. Upon further increase of x, T_c decreases. This variation of T_c with x is similar to that observed in many other high-T_c superconducting systems, for example, in $La_{2-x}Sr_xCuO_4$.[8] It can also be seen from the figure that the metallic property of the material decreases as x increases. For x=0.8, it shows a semimetallic behavior with T_c=38 K. For x=1.0, the resistance increases as the temperature decreases from 300 K and reaches a maximum at 23 K. Below 23 K, it decreases with decreasing temperature but does not reach zero resistance above 10 K. This behavior of resistance with temperature in $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ suggests that this system undergoes a metal-semiconductor transition with increasing concentration of Pr. This is consistent with the fact that the addition of electrons carried by Pr ions should reduce the hole concentration. Further, it is instructive to note that in this system, superconductivity is retained for a higher value (x=0.8) of Pr substitution. This should be compared and contrasted with a similar system $Pr_xCa_{1-x}Ba_2Cu_3O_7$, where superconductivity in bulk is not observed. Superconducting behavior of the $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ system is similar to that of $TlSr_2Ca_{1-x}R_xCu_2O_7$ (R= La, Nd, Sm, Gd).[9] This suggests that the valence state of the Pr ion in $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ is +3, and Pr $4f$ orbitals do not seem to overlap with O $2p$–Cu $3d$ orbitals appreciably. In the $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ system, the material superconducts for x=0.6 with T_c=62 K, whereas for x=1.0 it is a semiconductor.

The temperature dependence of the magnetic susceptibility $\chi(T)$ of the semiconducting $TlSr_2TbCu_2O_7$ measured by a SQUID magnetometer is shown in Fig. 3.

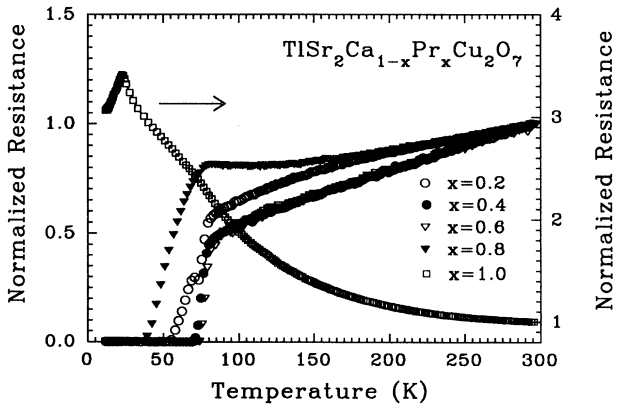

FIG. 2. Normalized resistance as a function of temperature for $TlSr_2Ca_{1-x}Pr_xCu_2O_7$. The samples with x=0.2, 0.4, 0.6, and 0.8 are superconducting with T_c=58, 70, 74, and 38 K, respectively. For x=1.0, the sample shows semiconducting behavior and a drop in resistance below 23 K.

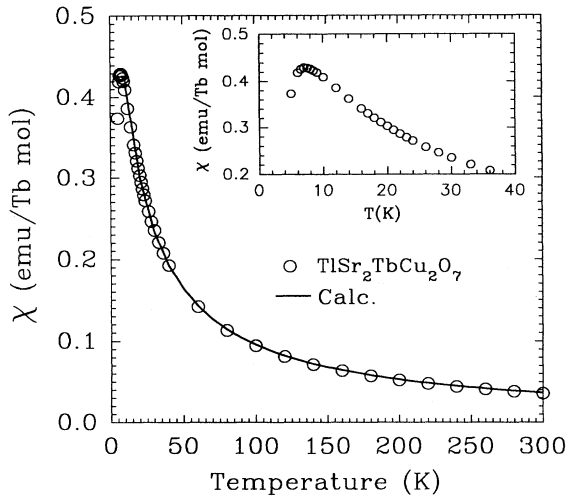

FIG. 3. Observed magnetic susceptibility for $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ with x=1.0 (○) in the temperature range of 4–300 K. The magnitude of the susceptibility for both $x = 1.0$ and 0.6 is the same in the temperature range of 100–300 K. The solid line is the result of the calculation based on the crystal field and exchange parameters (see text). The inset of the figure shows the antiferromagnetic ordering of the Tb moments in nonsuperconducting $TlSr_2TbCu_2O_7$ at 7.0 K.

From these results, it is seen that Tb moments order antiferromagnetically below 7.0 K. This T_N is higher than that for the only other known Tb-containing high-T_c related cuprate, $Pb_2Sr_2TbCu_3O_8$ (T_N=5.5 K) reported so far.[10] The Tb-Tb internuclear distances in $TlSr_2TbCu_2O_7$ and $Pb_2Sr_2TbCu_3O_8$ are 3.82 Å and 5.43 Å, respectively. This difference between the Tb-Tb distances is too large to explain the observed T_N values on the basis of dipole-dipole interactions. Perhaps other effects such as the superexchange mechanism invloved in the Tb-Tb interactions are also responsible for the observed values of T_N.

ac-χ measurements were made on the superconducting $TlSr_2Ca_{0.4}R_{0.6}Cu_2O_7$ with R=Pr and Tb, to look for any anomaly due to possible ordering of Pr and Tb moments. In both the systems, the diamagnetic signal was nullified at 10 K. The results of these measurements are shown in Figs. 4 and 5, respectively. It can be seen from these figures that there is a broad peak for both Pr and Tb samples centered at about 5 K and 6.2 K, respectively. These are attributed to the ordering of the Pr and Tb moments in the superconducting $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ and $TlSr_2Ca_{0.4}Tb_{0.6}Cu_2O_7$, respectively.[7] As already mentioned, $TlSr_2PrCu_2O_7$ does not form as a pure phase, and in its Ba analog, $TlBa_2PrCu_2O_7$, Pr moments order antiferromagnetically at 8.0 K.[11] A comparison of our earlier results[7] on Ba- and Sr-based Gd systems suggests that if the Sr-based Pr system had formed as single phase, the value of T_N would be expected to be more than that observed in the Ba-based Pr system. Lower values of T_N (=5 and 6.2 K, respectively) in the superconducting compounds $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ and

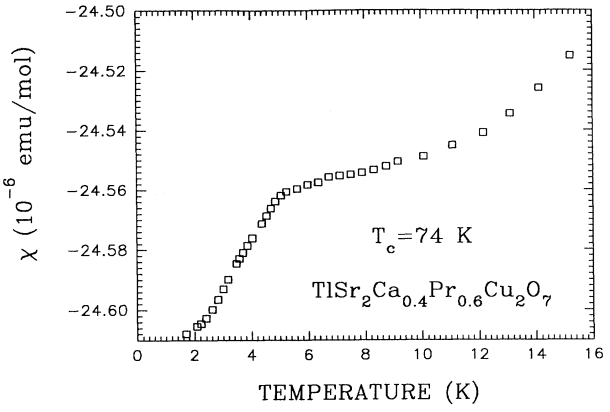

FIG. 4. The low-temperature part of the ac susceptibility of superconducting $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ (T_c=74 K). A broad peak centered at 5 K shows the antiferromagnetic ordering of the Pr^{3+} moments.

$TlSr_2Ca_{0.4}Tb_{0.6}Cu_2O_7$ are consistent with the fact that only 60% of Pr and Tb is present in these materials compared to 100% in $TlSr_2RCu_2O_7$ (T_N>8.0 and 7.0 K) with R=Pr and Tb, respectively.

Variation of the paramagnetic susceptibility of $TlSr_2Ca_{1-x}R_xCu_2O_7$ [R = Pr (x = 0.6), Tb (x=1.0, 0.6)] with temperature follows the Curie-Weiss behavior in the temperature range of 100 to 300 K, $\chi = C/(T + \theta_P)$, where C is the Curie-Weiss coefficient, which is related to the effective magnetic moment μ_{eff} as $C = N\mu_{\text{eff}}^2/3k_B$, and θ_P is the Curie-Weiss temperature. The values of μ_{eff} and θ_P are listed in Table I.

The values of the effective magnetic moments obtained from the Curie-Weiss fit to the magnetic susceptibility for $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ (x= 0.6 and 1.0) compounds are $9.53\mu_B$ and $9.68\mu_B$, respectively, which are close to that of Tb^{3+} ($9.72\mu_B$). This suggests that the contribution, if any, to the magnetization resulting from Cu^{2+} moments is negligible because of antiferromagnetic ordering of copper moments in the temperature range of the present in-

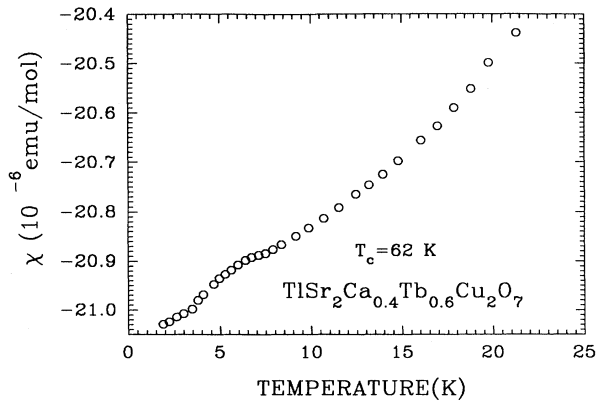

FIG. 5. The low-temperature part of the ac susceptibility of superconducting $TlSr_2Ca_{0.4}Tb_{0.6}Cu_2O_7$ (T_c=62 K). A broad peak centered around 6.2 K shows antiferromagnetic ordering of the Tb^{3+} moments.

TABLE I. Magnetic and superconducting data of $TlSr_2Ca_{1-x}R_xCu_2O_7$.

R	x	T_N(K)	μ_{eff} (μ_B)	θ_P (K)	T_c (K)
Pr	0.6	5.0	3.15	42	74
Tb	0.6	6.2	9.53	21	62
Tb	1.0	7.0	9.68	24	NS[a]

[a]NS indicates no superconductivity.

vestigation. This also implies that Cu-magnetic ordering is also not affected by the applied magnetic field. The θ_P values for $x = 1.0$ and 0.6, 21 K and 24 K, respectively, which are much higher than the observed Néel temperatures, further suggest the effect of crystalline electric fields at the R site.

The value of the effective magnetic moment ($=3.15\mu_B$) obtained from the Curie-Weiss fit to the magnetic susceptibility for the $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ compound, lie between the free-ion values expected for Pr^{3+} ($3.58\mu_B$) and Pr^{4+} ($2.54\mu_B$). This intermediate value of the effective magnetic moment between Pr^{3+} and Pr^{4+} has very often been used as an indication of mixed-valent behavior of Pr. However, from detailed studies on inelastic neutron scattering, magnetic susceptibility, and the heat capacity of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds, it is concluded that the spectroscopic, magnetic, and thermal properties of these compounds can be understood by crystal-field splitting of the Pr^{3+} ion.[4] The fact that the $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ compound is superconducting with a high T_c(=74 K), similar to that of other trivalent rare earths, indicates that the Pr ions are in a trivalent state. Thus, the low magnetic moment observed in our Pr-based compound should be understood on the basis of crystalline electric field effects.

IV. ANALYSIS OF MAGNETIC SUSCEPTIBILITY DATA

To obtain a better insight into the nature of the valence state of the Pr and Tb ions, we have systematically analyzed the experimental observations of magnetic susceptibility by taking into account the effect of the crystalline electric field and the exchange interaction. The Hamiltonian of the system consisting of the spin-orbit coupling, crystalline electric field, and Zeeman and exchange field terms,

$$\mathcal{H} = \lambda \mathbf{L}\cdot\mathbf{S} + \mathcal{H}_c + \beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S}) + \mathcal{H}_{\text{ex}}, \qquad (1)$$

is diagonalized within the substates arising from all the three lowest multiplets of Pr^{3+} (^{3}H, $J = 4$, 5, and 6) and all the seven lowest multiplets of Tb^{3+} (^{7}F, $J = 6$, 5, 4, 3, 2, 1, and 0) to obtain the energy and eigenfunctions of the respective ions.

In $TlSr_2Ca_{1-x}R_xCu_2O_7$, the rare-earth ions occupy only one site with a tetragonal site symmetry. The crystal field with tetragonal symmetry is characterized by five real parameters. The limited experimental data prevents us from the independent determination of all the five crystalline-field parameters unambiguously. Previous experimental and theoretical studies on $RBa_2Cu_3O_{7-\delta}$-type superconducting as well as nonsuperconducting compounds reveal that the crystal field at site R is predominantly cubic. Therefore, we assume that the overall features of the crystalline electric field potential can be reasonably described by retaining the parameters of cubic symmetry.

The crystal-field Hamiltonian in terms of tensor operators $C_m^{(n)}$ for cubic symmetry can be written as[12]

$$\mathcal{H}_c = B_4\sum[C_0^{(4)} + (5/14)^{\frac{1}{2}}(C_{-4}^{(4)} + C_{+4}^{(4)})] + B_6\sum[C_0^{(6)} - (7/2)^{\frac{1}{2}}(C_{-4}^{(6)} + C_{+4}^{(6)})] \qquad (2)$$

where B_4 and B_6 determine the strength of the cubic-crystal field. In cubic symmetry with eight coordination, the signs of B_4 and B_6 would be negative and positive, respectively. The matrix elements of $C_m^{(n)}$ between different states were calculated using the method given by Wybourn.[12]

The exchange interaction, in the molecular-field framework, above Néel temperature is given by

$$\mathcal{H}_{\text{ex}} = -2zJ\langle\mathbf{S}\rangle\cdot\mathbf{S}. \qquad (3)$$

Here z is the number of nearest equivalent neighbors interacting with the exchange interaction J, and $\langle S\rangle$ is the expectation value of the spin operator S. An iterative procedure is used to calculate $\langle S\rangle$ self-consistantly. The details of this procedure have been discussed by Marathe and Mitra.[13]

The calculated magnetic susceptibility agrees very well with the experimentally observed data of $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ in the entire temperature range of 100–300 K for $B_4 = -2620$ cm^{-1} and $B_6 = 2650$ cm^{-1} (see Fig. 6). The calculated crystalline electric-field level scheme for $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ is shown in Fig. 7.

The reduced value of the effective magnetic moment of the Pr^{3+} ion in $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ can be conceived in terms of rather unusual crystal-field splitting of the lowest electronic energy levels, similar to that

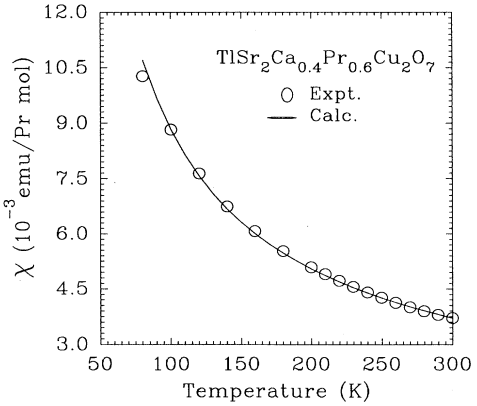

FIG. 6. Experimental (○) and calculated (solid line) magnetic susceptibility of superconducting $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$. The solid line is the result of the calculation based on the crystal-field parameters for Pr^{3+} ion.

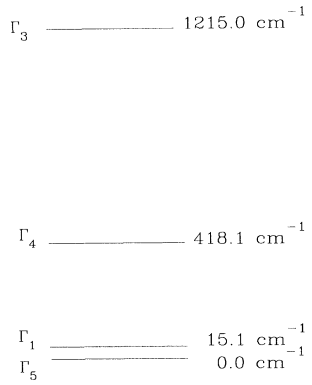

FIG. 7. Crystal-field level scheme for the ground state, J=4, of the Pr^{3+} ion for $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$, calculated using the crystal-field parameters $B_4 = -2620$ cm^{-1} and $B_6 = 2650$ cm^{-1}.

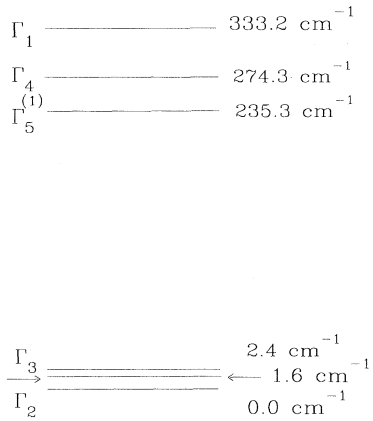

FIG. 8. Crystal-field level scheme for the ground state J= 6 of the Tb^{3+} ion for $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ with $x = 1.0$ and 0.6, calculated using the crystal-field parameters $B_4 = -2100$ cm^{-1} and $B_6 = 800$ cm^{-1}.

of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[14–16] The main feature of this set of crystal-field levels of $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ is two close low-lying energy levels, a triplet and a singlet, with the next higher levels above 421 cm^{-1}. In the temperature range 80–300 K, this low-lying triplet and singlet predominantly contribute to the temperature-dependent magnetic susceptibility. A similar kind of crystal-field level splitting has been observed for the $PrBa_2Cu_3O_{7-\delta}$ system, in which three levels (singlets) are very close to each other forming a quasitriplet with the next level above 400 cm^{-1}. The large value of the sixth-order crystal-field parameter is basically due to the approximations involved in assuming cubic symmetry. Our analysis of the magnetic-susceptibility data for $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ shows that there is no need to invoke the tetravalent or mixed-valent behavior of Pr to account for the reduced effective magnetic moment in this compound, and it can be explained in terms of crystal-field splitting of the ground multiplet of Pr^{3+} ion.

The calculated magnetic susceptibility agrees very well with the experimentally observed data of $TlSr_2TbCu_2O_7$ in the entire temperature range of 8–300 K for $B_4 = -2100$ cm^{-1}, $B_6 = 800$ cm^{-1} and $zJ = -1.63$ cm^{-1}. The calculated and the experimentally observed magnetic susceptibilities are shown in Fig. 3. The calculated crystal-field level scheme for $TlSr_2TbCu_2O_7$ is shown in Fig. 8. We observe that the magnitude of the magnetic susceptibility of $TlSr_2Ca_{0.4}Tb_{0.6}Cu_2O_7$ compound above the superconducting transition temperature is almost the same as that of the nonsuperconducting $TlSr_2TbCu_2O_7$ compound; thus the crystal-field effects in both the compounds are similar, and the data can be fitted with the same crystal-field parameters and zJ= 0.0.

V. CONCLUSION

The resistivity measurements on the $TlSr_2Ca_{1-x}Pr_xCu_2O_7$ system indicate that, except for x= 1.0, these are superconducting with T_c = 58,70,74,38 K for x=0.2,0.4,0.6,0.8, respectively. The variation of T_c with increasing Pr concentration suggests that the Pr ions are in the trivalent state. The system $TlSr_2Ca_{1-x}Tb_xCu_2O_7$ superconducts for $x = 0.6$ with T_c = 62 K, and for x=1.0 it becomes a semiconductor. Magnetic susceptibility measurements on the $TlSr_2TbCu_2O_7$ compound show that Tb magnetic moments order antiferromagnetically at 7.0 K. This is the highest magnetic ordering temperature observed among the known Tb-containing high-T_c related compounds. From ac-susceptibility measurements, it is inferred that the Pr and Tb magnetic moments in $TlSr_2Ca_{0.4}R_{0.6}Cu_2O_7$ order antiferromagnetically at 5.0 and 6.2 K, respectively, coexisting with superconductivity. The observed low magnetic moment of Pr ions ($3.15\mu_B$) in $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_7$ is explained in terms of the crystal-field splitting of the ground multiplet of Pr^{3+} ion.

ACKNOWLEDGMENTS

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