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Anisotropic Magnetic and Calorimetric Properties of the Incommensurate Modulated $Bi_2Sr_2PrCu_2O_{8+\delta}$ Single Crystal

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Anisotropic magnetic and calorimetric properties of the incommensurate modulated $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystals have been reported. No Pr magnetic ordering was observed down to 0.5 K in specific heat data and in anisotropic magnetic susceptibility measurements for magnetic field applied along the single crystal orthorhombic ab-plane or c-axis. In comparison, isostructural Gd polycrystalline sample $Bi_2Sr_2GdCu_2O_{8+\delta}$ exhibits an antiferromagnetic order with Néel temperature T_N(Gd) of 1.7 K. The $Bi_2Sr_2PrCu_2O_{8+\delta}$ compound represents the first example of no Pr anomaly observed for all two-CuO_2-layers Pr cuprates $M_mA_2PrCu_2O_y$ (M = Hg, Pb, Tl, Bi, Nb, Cu; A = Ba, Sr; m = 1, 2, 3). The lack of Pr ordering is believed to be due to a very weak quasi-2D Pr-0-Pr superexchange interaction caused by the strong structural modulation.

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I. Introduction

Since the discovery of anomalously high Pr antiferromagnetic ordering of 10 - 17 K for the Cu-1212-type (or commonly known as the 123-type) $PrBa_2Cu_3O_{7-y}$ system ($0 \leq y \leq 1$) [1-5], many new Pr cuprates with the similar Pr anomaly were observed and reported for the two-CuO_2-layer M-1212-type $MA_2PrCu_2O_7$ systems (M = Hg, Pb, Tl, Nb, Cu; A = Ba, Sr), with T_N(Pr) values ranging from 4 to 12 K [6-10].

The Pr anomalies with T_N(Pr) of 6-14 K were also observed in the new two-CuO_2-layer M-3212-type $(Pb_2Cu)(Ba,Sr)_2PrCu_2O_8$ system (or commonly known as the 2213-type $Pb_2(Ba,Sr)_2PrCu_3O_8$) [5,11].

Since in high-T_c cuprates, a total replacement of divalent Ca by rare earth between the CuO_2 layers can be achieved so far only in the two-CuO_2-layer m212-type $M_mA_2RCu_2O_y$ (m = 1, 2, 3; R = rare earth) structures, questions arise as whether the anomalous Pr effect occurs with m = 2. In deed, two new M-2212-type systems with Pr anomaly were reported recently: the (Pr,Cu)-2212-type$(Pb,Cu)_2(Ba,Sr)_2PrCu_2O_8$ compound with $T_N(Pr)$ of 9 K [12] and the Cu-2212-type (or commonly known as the 124-type)$PrBa_2Cu_4O_8$ with $T_N(Pr)$ of 18 K [13].

However, for the new Bi-2212-type $Bi_2Sr_2PrCu_2O_8$ compound with the $Bi_2Sr_2CaCu_2O_8$-type structure, no Pr anomalies down to 1.6 K were reported for polycrystalline sample [14]. In order to solve this puzzle, single crystal $Bi_2Sr_2PrCu_2O_8$ were grown using the floating zone technique for the detailed studies of anisotropic magnetic properties of this peculiar compound.

II. Experimentals

Polycrystalline samples with the nominal composition $Bi_2Sr_2RCu_2O_{8+\delta}$ (R = Pr, Gd, Y) were prepared by solid-state reaction techniques. High-purity $Bi_2O_3, SrCO_3, R_2O_3$ and CuO powders with the ratio Bi:Sr:R:Cu = 2:2:1:2 were well-mixed first, ground and calcined at 750-820 °C in air for one week with intermediate grinding. The reacted powders were pressed into pellets and sintered at 890-920 °C in air or in flowing argon for 3 days, then quenched in liquid nitrogen.

Single crystals $Bi_2Sr_2PrCu_2O_{8+\delta}$ were grown using the floating zone method. High-purity $Bi_2O_3, SrCO_3, Pr_2O_3$ and CuO powders with the off-stoichiometrical ratio Bi:Sr:R:Cu = 2.6:2:1:1.8 were mixed, ground and calcined at 750-800 °C in air for three days. The reacted powders were pressed into cylinders and sintered at 850 °C in air, then put into the double ellipsoidal type halogen lamp floating zone oven for single crystal growth. Average size of the single crystals is 5 mm x 3 mm x 0.1 mm.

Powder and single crystal x-ray data were obtained with a Rigaku Rotaflex 18 kW rotating anode x-ray diffractometer using Cu K_α radiation with a scanning rate of 1° in 2% per minute. A Lazy-Pulverix-PC program was employed for phase identification and lattice parameter calculation. For the a-axis and b-axis x-ray diffraction measured in the transmission fashion, a fiber sample attachment with a divergence slit was used. Anisotropic magnetic susceptibility measurements were carried out with a Quantum Design MPMS or a $MPMS_2$ superconducting quantum interference device (SQUID) magnetometer from 2 to 400 K in an applied field of I kG. Low temperature specific heat measurements were made with a He^3 thermal relaxation calorimeter for polycrystdline samples down to 0.4 K or a He^4 calorimeter for single crystal down to 1.2 K.

III. Results and discussion

The powder x-ray diffraction pattern for the $Bi_2Sr_2PrCu_2O_{8+\delta}$ polycrystalline sample prepared in air is shown in Fig. 1. Except for the structural modulation and small amount of impurity lines, the diffraction pattern can be well indexed by the orthorhombic $Bi_2Sr_2CaCu_2O_8$-type structure with the unmodulated space group of the Fmmm or Amaa-type, and a strong incommensurate modulation along the orthorhombic b-axis [15]. The orthorhombic lattice parameters obtained for the powder sample are a = 5.478(5) A, b = 5.501(5) Å, c = 30.267(9) A, with a unit cell volume V of 912.1(9) Å^3. For the single crystal sample grown by the floating zone method, c-axis x-ray diffraction pattern in Fig. 2 indicates a clean pattern with the orthorhombic (001) lines having a slightly longer c parameter of 30.339(9) A. The b-axis diffraction pattern in Fig. 3 gives a longer b-parameter of 5.515(5) Å and an incommensurate modulation along the b-axis with period s = 4.16. No modulation was observed along the orthorhombic a-axis. The lattice parameter discrepancy between LN_2-quenched polycrystalline sample and single crystal is probably originated from different sample preparation conditions which resulted with higher oxygen content parameter δ in single crystal.

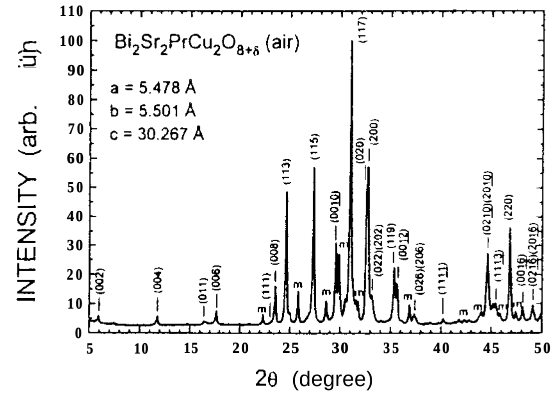

FIG. 1. Powder x-ray diffraction patterns of Bi-2212-type orthorhombic $Bi_2Sr_2PrCu_2O_{8+\delta}$ polycrystalline sample. Incommensurate modulation and impurity lines are indicated by *m*.

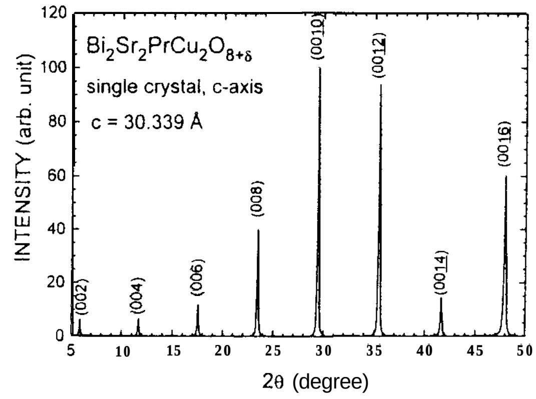

FIG. 2. X-ray diffraction patterns of orthorhombic (001) lines for $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystal.

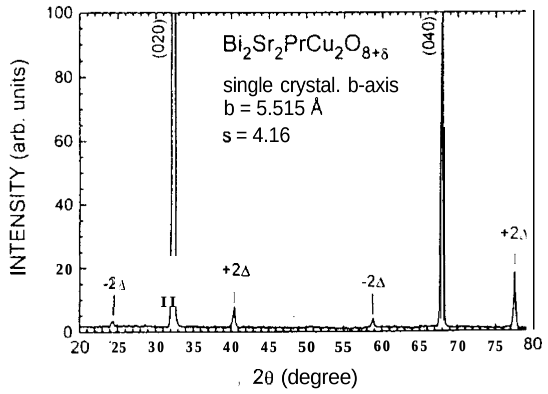

FIG. 3. X-ray diffraction patterns of orthorhombic (0*k*0) lines for $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystal. Incommensurate modulation lines were denoted by ● t2A.

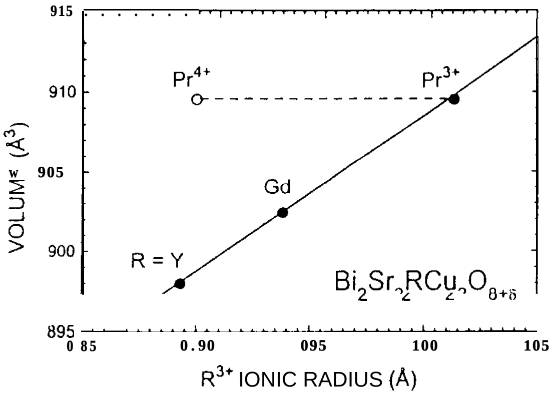

FIG. 4. Orthorhombic cell volume Vof polycrystalline $Bi_2Sr_2RCu_2O_{8+\delta}$ samples versus rare earth R^{3+} ionic radius (R = Pr, Gd, Y) and Pr^{4+} ionic radius.

The unit-cell volumes V for polycrystalline samples $Bi_2Sr_2RCu_2O_{8+\delta}$ (R = Pr, Gd, Y) in Fig. 4 follow a linear dependence with the R^{3+} ionic radius, indicating a predominately Pr^{3+} character in the Bi-2212-type Pr compound. The deviation of the Pr^{4+} point from this simple relation is apparent. This conclusion is consist-ent with the predominately Pr^{3+} character observed for all other Pr cuprates with two-CuO_2-layer [6, 8, 10-12].

The temperature dependence of anisotropic molar and inverse molar magnetic susceptibilities (χ_m and χ_m^{-1}) for $Bi_2Sr_2RCu_2O_{8+\delta}$ single crystal with 1 kG magnetic field applied in the ab-plane is shown in Fig. 5. Except for the small fluctuation observed around 330 K indicating a possible Cu^{2+} magnetic ordering, the data shows a simple Curie-Weiss fit χ_m --χ_c + $C/(T+\theta_p)$ = 1.54 x $10^{-3}+0.949/(T$ t 19.3) cm^3/mol which yields a large negative paramagnetic intercept θ_p = -19.3 K and an effective magnetic moment μ_{eff} of 2.75 μ_B per Pr if the small Cu^{2+} moment is neglected. For applied magnetic field along the c-axis, θ_p of -22.0 K and μ_{eff} of 3.34 μ_B were obtained. It is noteworthy that the c-axis effective moment of 3.34 μ_B is closer to the free Pr^{3+} ion value of 3.58 μ_B, while the ab-plane μ_{eff} of 2.75 μ_B is closer to Pr^{4+} value of 2.54 μ_B. These anisotropic effective moments reflect the strong directional hybridization between the Pr 4f and the eight O $2p_\pi$ orbitals in the adjacent CuO_2-layers.

The large negative paramagnetic intercept θ_p indicates a possible long-range antiferromagnetic Pr ordering at low temperature. However, the low temperature specific heat C(T) and differential molar magnetic susceptibility $d\chi_m/dT$ data for $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystals in Fig. 6 indicate no Pr anomaly observed down to 1.2 K. For polycrystalline sample, no Pr anomaly was observed down to 0.5 K. Recent neutron diffraction data also indicates no extra Bragg peaks appear at this temperature range [16].

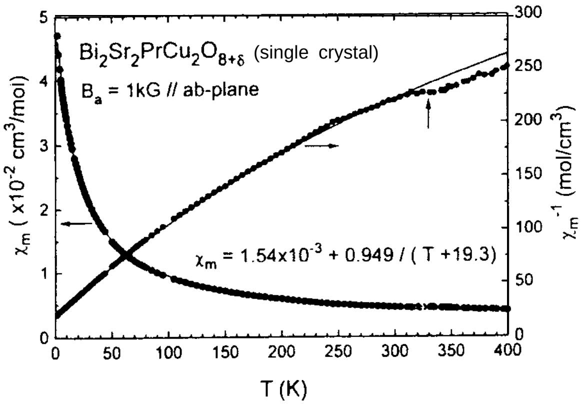

FIG. 5. Temperature dependence of anisotropic molar magnetic susceptibility χ_m and inverse susceptibility χ_m^{-1} with applied magnetic field B_a parallel to the ab-plane of $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystal.

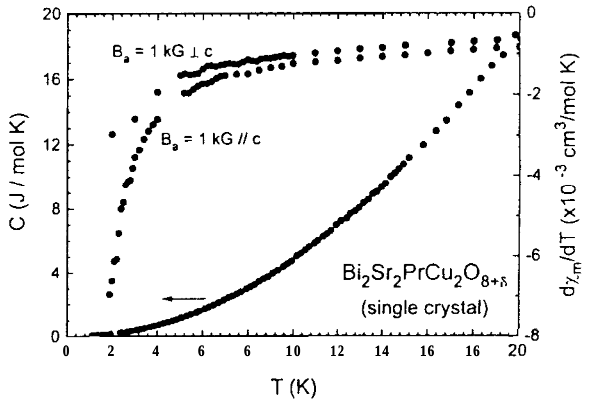

FIG. 6. Low temperature specific heat $C(T)$ and anisotropic differential molar magnetic susceptibility $d\chi_m/dT$ for $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystal.

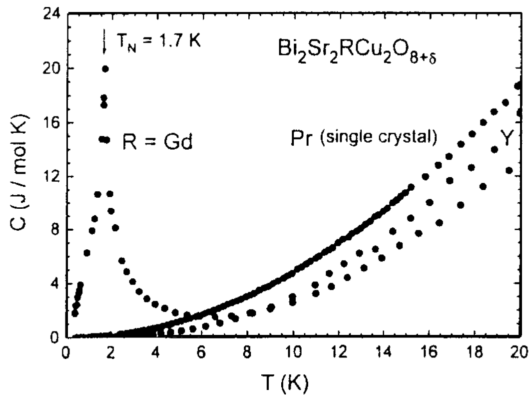

Fig. 7. Temperature dependence of specific heat C(T) for $Bi_2Sr_2RCu_2O_{8+\delta}$(R=Pr, Gd, Y).

The absence of Pr anomaly at low temperature can be more clearly apprehended through comparing the low temperature specific heat data for three rare earth compounds $Bi_2Sr_2RCu_2O_{8+\delta}$ (R = Pr, Gd, Y). As shown collectively in Fig. 7, contrary to Pr compound, a T_N(Gd) of 1.7 K with a well-defined X-type transition was observed for isostructural $Bi_2Sr_2GdCu_2O_{8+\delta}$ compound [17]. The magnetic entropy S_m derived from C/T versus T data for Gd compound is close to 90% of expected Rln8 value for Gd^{3+} moments with $J = S = 7/2$. However, T_N(Gd) of 1.7 K is also smaller than 2.2-2.3 K commonly observed for all other Gd cuprates with two-CuO_2-layer [18], indicating a weaker magnetic interaction for the Gd compound. No transition was observed for non-magnetic Y compound $Bi_2Sr_2YCu_2O_{8+\delta}$ at low temperature.

The reason that for lack of Pr long range magnetic ordering down to 1.4 K for Pr compound is probably due to a weaker quasi-2D Pr-0-Pr superexchange interaction caused by the strong structural modulation. Since Pr is one of the lightest elements of rare-earth series, its 4f wave functions should be more extended. The anomalously high T_N(Pr) in other Pr cuprates indicates the importance of the quasi-2D Pr-0-Pr superexchange mechanism through the strong hybridization between the Pr 4f and the eight 0 $2p_\pi$ orbitals in the adjacent CuO_2 layers [19]. This degree of hybridization can be readily reflected in the Pr-0 bond length. As a consequence, Pr ordering temperature T_N(Pr) for the M-1212 systems decrease monotonically with increasing Pr-0 bond length, from 2.443 Å for 17 K $PrBa_2Cu_3O_7$ to 2.514 Å for 4 K $TlSr_2PrCu_2O_7$ [10,20-21]. Whether the lack of Pr anomaly is the direct result of longer Pr-0 bond length remained to be checked. Another possibility is that the Pr moments will eventually order below 0.5 K. Detailed single crystal structural study and ultra-low temperature studies are in progress to check these possibilities.

IV. Conclusion

Magnetic and calorimetric data were reported for the incommensurate modulated Bi-2212-type $Bi_2Sr_2PrCu_2O_{8+\delta}$ single crystal grown by the floating zone method. No T_N(Pr) was observed down to 0.5 K for magnetic field applied along the single crystal ab-plane or c-axis. In comparison, isostructural Gd sample $Bi_2Sr_2GdCu_2O_{8+\delta}$ exhibits a T_N(Gd) of 1.7 K. The $Bi_2Sr_2PrCu_2O_{8+\delta}$ compound represents the first example of the lack of Pr anomaly for all Pr cuprates reported.

Acknowledgments

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