Anisotropic Gd magnetism in $TlSr_2GdCu_2O_{7-\delta}$, $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$, and $Pb_2Sr_2GdCu_3O_{8+y}$

C. C. Lai and J. H. Shieh
Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

B. S. Chiou
Institute of Electronics, National Chaio Tung Unviersity, Hsinchu, Taiwan 300, Republic of China

J. C. Ho
Department of Physics, Wichita State University, Wichita, Kansas 67208

H. C. Ku
Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China
(Received 20 July 1993; revised manuscript received 17 September 1993)

Magnetic and calorimetric measurements reveal antiferromagnetic ordering of Gd^{3+} ions in the tetragonal compounds $TlSr_2GdCu_2O_{7-\delta}$ and $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$, as well as in the vacuum-annealed orthorhombic compound $Pb_2Sr_2GdCu_3O_{8+y}$ ($y \cong 0$). The Néel temperatures T_N(Gd) of 2.3–2.4 K of these semiconducting compounds are almost identical to those for several other high-T_c Gd cuprates, with similar double-CuO_2-layer structures. Correlation of T_N with the Gd-Gd distance in various Gd cuprate systems indicates a highly anisotropic magnetic coupling. By taking into account another common feature in terms of a broad Schottky-like specific heat below T_N, the expected magnetic entropy of $R \ln(2J+1) = R \ln 8$ can be obtained.

Rare-earth magnetism in high-T_c cuprate systems has been the subject of extensive research in recent years. Apart from anomalous Pr ordering in $PrBa_2Cu_3O_{7-y}$ (Ref. 1) and $TlBa_2PrCu_2O_{7-\delta}$ (Ref. 2) with many puzzling characteristics, Gd received the earliest attention through its antiferromagnetic ordering in both superconducting $GdBa_2Cu_3O_7$ (1:2:3:7) and nonsuperconducting $GdBa_2Cu_3O_6$ (1:2:3:6).[3,4] Somewhat unexpected, they exhibit identical Néel temperatures T_N near 2.2 K. In contrast, T_N is sensitive to the oxygen content in other isostructural $RBa_2Cu_3O_{7-\delta}$ compounds with R being, e.g., Pr or Nd.[5] The whole issue is yet to be fully resolved, and experiments on more diversified high-T_c cuprate systems are in order. This work is indeed carried out for such purposes. It extends our earlier study on tetragonal $TlBa_2GdCu_{7-\delta}$ Tl(1:2:1:2) (Ref. 6) to three new Gd-containing compounds, all with Sr substituting for Ba. In these three compounds, $TlSr_2GdCu_2O_{7-\delta}$ and $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$ are isostructural to $TlBa_2GdCu_2O_{7-\delta}$, while $Pb_2Sr_2GdCu_3O_{8+y}$ Pb(2:2:1:3) is an orthorhombic compound.[7] Of particular interest is the correlation of their Néel temperatures with the Gd-Gd distance. To supplement magnetic data, calorimetric measurements allow magnetic entropy determination. Gd^{3+} has zero orbital angular momentum L and, therefore, experiences no crystal-field effect. The total angular momentum J is equal to the total spin $S=\frac{7}{2}$. Consequently, the $2J+1$ ground-state multiplet remains fully degenerate in the absence of magnetic ordering, and a magnetic entropy of $R \ln 8$ is expected to be associated with the ordering process. Sample preparation method and experimental details were described elsewhere.[6]

The x-ray powder diffraction pattern of the $TlSr_2GdCu_2O_{7-\delta}$ ($\delta < 0.2$) sample indicates a single-phase Tl(1212) or $TlBa_2CaCu_2O_{7-\delta}$-type structure[2] with tetragonal lattice parameters $a=3.831(2)$ Å and $c=12.040(5)$ Å. This structure with space group $P4/mmm$ is very much similar to that of the tetragonal $GdBa_2Cu_3O_6$ (space group $P4/mmm$) or orthorhombic $GdBa_2Cu_3O_7$ (space group P/mmm). In fact, its only difference from $GdBa_2Cu_3O_7$ is the replacement of the Cu-O chains by a Tl-O plane with oxygen located at the center. An oxygen deficiency parameter $\delta < 0.2$ is estimated based on the Rietveld refinement result of the isostructural compound $TlSr_2PrCu_2O_{7-\delta}$.[8] A slight deficiency of Tl($<5\%$) is also estimated and is due to the sample preparation process.[8]

The temperature dependence of specific heat C of $TlSr_2GdCu_2O_{7-\delta}$ is shown in Fig. 1, along with the earlier data for the isostructural and nonmagnetic $TlBa_2YCu_2O_{7-\delta}$ (Ref. 2) to simulate the lattice contribution $C_l \cong \beta T^3 = 0.0016 T^3$ corresponding to a Debye temperature θ_D 0f 250 K. A well-defined Gd ordering peak prevails just below 2.4 K, in agreement with the low-temperature magnetic susceptibility χ data with T_N (Gd) $=2.4\pm0.1$ K in the inset. High-temperature magnetic susceptibility data indicate an antiferromagnetic ordering of Cu^{2+} moments above room temperature. A Curie-Weiss behavior $\chi = C^*/(T-\theta_p)$ was observed at low temperature in the 1 T field, where the strong applied magnetic field effectively decouples the weak exchange coupling between the disordered Gd^{3+} and ordered Cu^{2+} moments. The Curie constant $C^* = N\mu_{\text{eff}}^2/3k$ corresponds to an effective magnetic moment $\mu_{\text{eff}} = 7.7\mu_B$, a

0163-1829/94/49(2)/1499(4)/$06.00

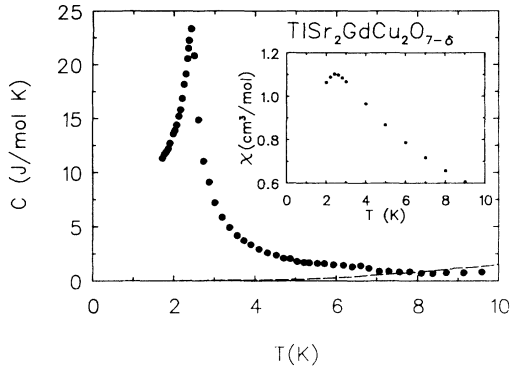

FIG. 1. Temperature dependence of specific heat C and molar magnetic susceptibility χ (inset) of $TlSr_2GdCu_2O_{7-\delta}$. The dashed line is the specific heat of $TlBa_2YCu_2O_{7-\delta}$, which provide the estimate of lattice contribution.

value close to $7.94\mu_B$ for the free Gd^{3+} ion ($J=S=\frac{7}{2}$), if the small contribution from Cu^{2+} moments are neglected. The paramagnetic Curie-Weiss intercept at $\theta_p=-3.2$ K is close to T_N, except for the sign, in agreement with antiferromagnetic interactions. The difference between this T_N(Gd) and the equivalent value of 2.3 ± 0.1 K for isostructural $TlBa_2GdCu_2O_{7-\delta}$ (Ref. 6) will be discussed later.

Figure 2 presents the specific-heat data in a different format of C_m/T versus T, where $C_m=C-C_1$. Integration over the area below the data point and the dashed-line extrapolation yields the magnetic entropy $S_m(T)=\int_0^T(C_m/T)dT$. The expected total magnetic entropy $R\ln 8$ is being approached not far above T_N as shown in the inset. It implies that the broad shoulder-type extrapolation below 2 K has certain validity. Indeed, this can be well justified because similar features have been observed in several other Gd-containing high-T_c cuprates.[6]

For isostructural Pb(1212) compound $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$ ($\delta<0.2$), powder x-ray-diffraction analysis confirmed the formation of a single-phase Pb(1212) with $a=3.839(2)$ Å and $c=11.838(5)$ Å. The Tl ($1a$) sites of space group $P4/mmm$ are now occupied by equal numbers of Pb and Cu. Calorimetric and magnetic data in Fig. 3 resemble those in Fig. 1 for $TlSr_2GdCu_2O_{7-\delta}$ and an antiferromagnetic ordering prevails at 2.3 K. Magnetic susceptibility above T_N shows a Curie-Weiss behavior, with an effective magnetic moment $\mu_{\rm eff}=7.8\mu_B$ and a paramagnetic intercept of $\theta_p=-2.4$ K. Following the further analysis in Fig. 4 by assuming the same lattice contribution $C_1=0.0016T^3$ in calculating magnetic specific heat $C_m=C-C_1$ and a low-temperature Schottky-type specific-heat anomaly, a total magnetic entropy $S_m\simeq R\ln 8$ is derived. It supports unequivocally that the observed transition is indeed associated with the Gd^{3+} ions, further confirming that the Tl-O or (Pb,Cu)-O planes do not participate significantly toward the ordering process.

A parallel study was performed on the vacuum annealed compound $Pb_2Sr_2GdCu_3O_{8+y}$ ($y\cong 0$). Powder x-ray diffraction data indicate a single-phase orthorhombic Pb(2213) or $Pb_2Sr_2YCu_3O_{8+y}$-type structure ($0\le y\le 1$),[7] with lattice parameters $a=5.411(3)$ Å, $b=5.448(3)$ Å, and $c=15.742(5)$ Å. The main difference between $Pb_2Sr_2GdCu_3O_8$ and $TlSr_2GdCu_2O_7$ is the replacement of the Tl-O plane by the PbO-Cu-PbO planes. Magnetic and calorimetric data for this sample are shown in Figs. 5 and 6, respectively. A small lattice specific heat C_1 of $0.0019T^3$ is calculated based on the assumption of the same Debye temperature θ_D of 250 K. Again, a T_N of 2.3 K is obtained. Magnetic susceptibility above T_N shows a Curie-Weiss behavior, with an effective magnetic moment $\mu_{\rm eff}=7.8\mu_B$ and a Curie-Weiss intercept of $\theta_p=-3.6$ K. A total magnetic entropy $S_m\simeq R\ln 8$ is derived.

Having shown that T_N(Gd) for the three compounds studied here remains practically the same at 2.3–2.4 K, it can be stated that there is no significant difference in their overall magnetic interaction strength among Gd moments. In fact, the Gd sublattice is relatively simple, with the Gd-Gd nearest-neighbor in the ab basal plane. The nearest-neighbor distance r_1 is equal to a of 3.83–3.84 Å for $TlSr_2GdCu_2O_{7-\delta}$ and

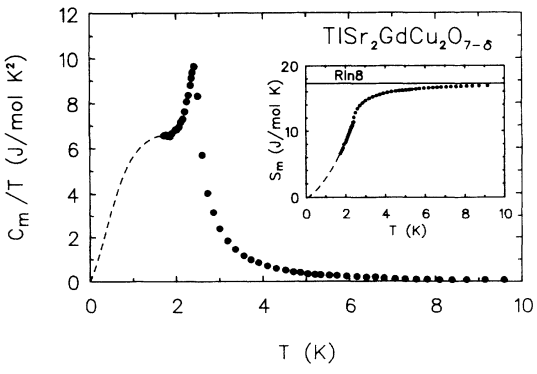

FIG. 2. Temperature dependence of magnetic C_m/T and magnetic entropy S_m (inset) of $TlSr_2GdCu_2O_{7-\delta}$. The area integral below the $C_m/T-T$ plot yields S_m, while it approaches the expected value of $R\ln 8$ just above T_N. The broad shoulder extrapolation of C_m/T at lower temperatures is explained in the text.

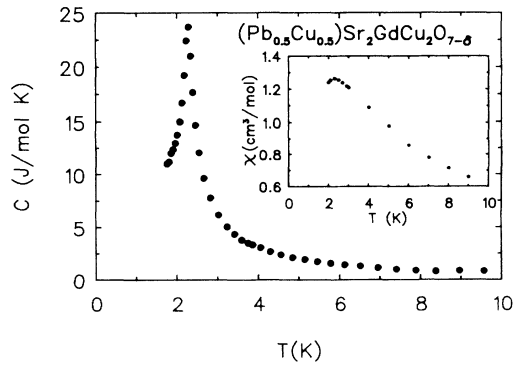

FIG. 3. Temperature dependence of specific heat C and molar magnetic susceptibility χ (inset) of isostructural $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$.

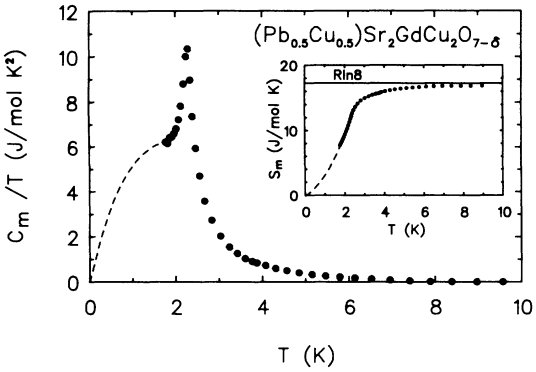

FIG. 4. Temperature dependence of magnetic C_m/T and magnetic entropy S_m (inset) of $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$.

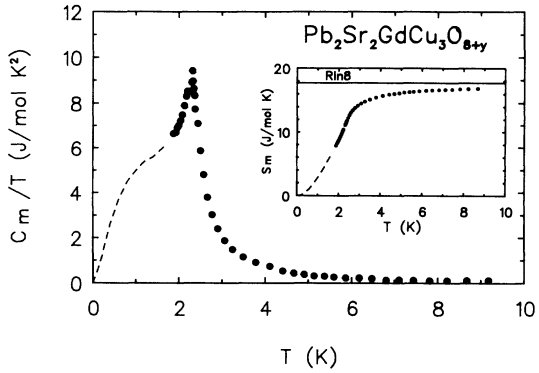

FIG. 6. Temperature dependence of magnetic C_m/T and magnetic entropy S_m (inset) of $Pb_2Sr_2GdCu_3O_{8+y}$.

$(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$ and

$$r_1=(a^2+b^2)^{1/2}=3.85 \text{ Å}$$

for $Pb_2Sr_2GdCu_3O_{8+y}$. The shortest Gd-Gd distance along the c-axis d_c is extremely long. For $TlSr_2GdCu_2O_{7-\delta}$ and $(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$, $d_c=11.8-12.0$ Å and is the seventh nearest-neighbor distance r_7. For $Pb_2Sr_2GdCu_3O_{8+y}$, $d_c=15.7$ Å is the ninth nearest-neighbor distance r_9. Table I summarizes the Gd antiferromagnetic ordering temperature T_N(Gd) values for various Gd cuprates together with the tetragonal/orthorhombic lattice parameters, Gd-Gd nearest-neighbor distance (r_1) and the shortest Gd-Gd distance along the c axis (d_c), in the single CuO_2 layer compound Gd_2CuO_4 and $(Gd_{1.85}Ce_{0.15})CuO_4$.[9] The nearest-neighbor distance is pointed along the c axis with $r_1=d_c=3.552-3.570$ Å, where Gd^{3+} ions occupy the $(4e)(0,0,z=0.35)$ sites in space group $I4/mmm$. All other compounds with the double-CuO_2 layers have the nearest-neighbor distance in the basal plane $r_1=3.83-3.89$ Å and a very long Gd-Gd distance along or near the c axis. The comparison further suggests that the overall magnetic interaction is highly anisotropic and the interaction strength in the c direction is much weaker than that in the basal plane. Still, the magnetic order is 3D in nature, as verified by neutron-diffraction experiments in $GdBa_2Cu_3O_7$ and $GdBa_2Cu_3O_6$.[10,11] Realizing that the three compounds reported here, as well as $TlBa_2GdCu_2O_{7-\delta}$,[6] are practically semiconductors, magnetic dipole-dipole interaction is probably the major mechanism responsible for the magnetic ordering process. If the Gd magnetic structure is similar to that of $GdBa_2Cu_3O_7$,[10] then the dipole-dipole interaction energy among Gd^{3+} moments in the basal plane up to sixth nearest neighbors can be estimated using the formula

$$U_{d-d}\cong 4\mu^2(1/r_1^3-1/r_2^3-1/r_3^3+2/r_4^3+1/r_5^3+1/r_6^3)$$
$$=0.24 \text{ meV},$$

where $\mu(\text{Gd})\cong 7.9\mu_B$, $r_1\cong 3.84$ Å, $r_2=\sqrt{2}r_1$, $r_3=2r_1$, $r_4=\sqrt{5}r_1$, $r_5=\sqrt{8}r_1$, and $r_6=3r_1\cong 11.52$ Å. This value is still lower than the estimated exchanged energy

$$U_{ex}\cong 2\mathbf{J}\cdot S^2=0.47-0.72 \text{ MeV},$$

where the average exchange interaction parameter $\mathbf{J}$ is deduced from the Curie-Weiss paramagnetic intercept θ_p. Other coupling mechanisms (superexchange and/or RKKY coupling) must therefore play a complementary role. Although the major mechanism appears to be the dipole-dipole interaction, its intrinsic ansitropy does not seem to play any role here. The effective 2D character of this coupling simply arises from the long Gd-Gd distance along the c axis compared to that within the basal plane. The existence of other coupling mechanisms is revealed by (i) the 3D nature of the Gd magnetic ordering,[10,11] and (ii) by the enhancement of T_N(Gd) in Gd_2CuO_4 and $(Gd_{1.85}Ce_{0.15})CuO_4$,[9] which cannot be explained by the dipole-dipole interaction alone. The second coupling mechanism is probably very anisotropic, as suggested by the different T_N(Gd) values in Gd_2CuO_4 and related compounds.

The broad shoulder-type extrapolation below 2 K has certain validity because similar features have been observed in several other Gd-containing high-T_c cuprates.[6] Such a seemingly common behavior has been contemplated with several theoretical interpretations including, e.g., a 2D-3D ordering or a commensurate-incommensurate transition in magnetic order. However, neutron-diffraction data have shown that Gd ordering is a 3D

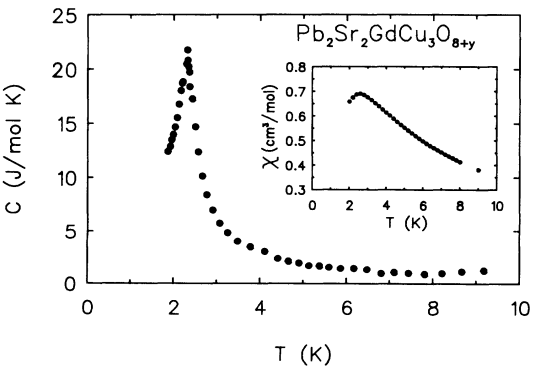

FIG. 5. Temperature dependence of specific heat C and molar magnetic susceptibility χ (inset) of $Pb_2Sr_2GdCu_3O_{8+y}$.

TABLE I. Gd Néel temperature T_N, tetragonal/orthorhombic lattice parameters (a,b,c), Gd-Gd nearest-neighbor distance (r_1) and the shortest Gd-Gd distance along the c axis (d_c) for various Gd cuprates.

System	Compound	T_N (K)	a (Å)	b (Å)	c (Å)	r_1 (Å)	d_c (Å)	Reference
T'(2:1:4)	Gd_2CuO_4	6.6	3.892		11.90	3.570	3.570	9
	$(Gd_{1.85}Ce_{0.15})CuO_4$	5.3	3.902		11.84	3.552	3.552	9
(1:2:3)	$GdBa_2Cu_3O_6$	2.2	3.877		11.81	3.877	11.81	4 and 10
	$GdBa_2Cu_3O_7$	2.2	3.844	3.905	11.71	3.844	11.71	3 and 11
(1:2:1:2)	$TlBa_2GdCu_2O_{7-\delta}$	2.3	3.888		12.48	3.888	12.48	6
	$TlSr_2GdCu_2O_{7-\delta}$	2.4	3.831		12.04	3.831	12.04	This work
	$(Pb_{0.5}Cu_{0.5})Sr_2GdCu_2O_{7-\delta}$	2.3	3.839		11.84	3.839	11.83	This work
(2:2:1:3)	$Pb_2Sr_2GdCu_3O_{8+y}$	2.3	5.411	5.448	15.74	3.850	15.74	This work
Bi(2:2:1:2)	$Bi_2Sr_2GdCu_2O_{8+y}$	1.6	5.441	5.468	30.19	3.857	15.34[a]	12

[a]For the Bi(2:2:1:2) phase, $d_c(\text{Gd-Gd}) > c/2$ is slightly off the c axis.

commensurate antiferromagnetic transition, it is unlikely that the commensurate to incommensurate transition can occur below the transition temperature. On the other hand, a 2D ordering should occur at higher temperature than a 3D ordering but not below it. It should be noted that similar broad peaks below magnetic transition temperature T_m were observed previously in ferromagnetic Gd metal and metallic $GdCu_2Si_2$ ($T_N = 11.9$ K).[13,14] Fishman and Liu proposed that the broad peak below T_m may be caused by the quantum spin fluctuations induced by a transverse degree of freedom[13]; the peak becomes more pronounced as the total spin S increases and occurs at temperature $T^* \simeq 3T_m/(S+1)$. For Gd^{3+} having the highest S value of $\frac{7}{2}$ among all rare-earth ions, $T^* \simeq 0.67T_N = 1.5$ K is estimated and is in reasonable agreement with our experimental observations. However, Fishman and Liu did not contribute the bump in the Gd metal to this quantum fluctuation, but to a normal mean-field mechanism.[13] Regardless of all these discrepancies that may be caused by different types of magnetic coupling, the main conclusion remains valid, namely, taking this Schottky-like bump into account is fundamental in the calculation of the magnetic entropy.

Several conclusions can thus be made.

(1) Antiferromagnetic ordering among Gd^{3+} ions is found to have a rather narrow Néel temperature range of 2.2–2.4 K in high-T_c Gd cuprates systems with double-CuO_2 layer structures. For single-CuO_2-layer compound Gd_2CuO_4, a higher T_N value was observed.

(2) Dipole-dipole interaction is mainly responsible for the ordering process, with other anisotropic coupling mechanisms (superexchange and/or RKKY) playing a complementary role.

(3) A Schottky-like anomaly in specific heat below the cooperative-type peak at T_N is a common feature for these Gd-containing compounds. It needs to be taken into account to derive the expected entropy $R\ln(2J+1) = R\ln 8$ associated with the ordering process.

We thank Dr. S. H. Liu for helpful discussions. This work at NTHU was supported by the National Science Council of the Republic of China under Contract Nos. NSC-82-0115-M007-010 and NSC-83-0212-M007-069.

[1]A comprehensive review can be found in H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).

[2]C. C. Lai, B. S. Chiou, Y. Y. Chen, J. C. Ho, and H. C. Ku, Physica C **202**, 104 (1992).

[3]J. C. Ho, P. H. Hor, R. L. Meng, C. W. Chu, and C. Y. Huang, Solid State Commun. **63**, 711 (1987).

[4]J. C. Ho, C. Y. Huang, P. H. Hor, R. L. Meng, and C. W. Chu, Mod. Phys. Lett. B **1**, 417 (1988).

[5]J. W. Lynn, in *High Temperature Superconductivity* (Springer-Verlag, Berlin, 1990), Chap. 8.

[6]Y. Y. Chen, C. C. Lai, B. S. Chiou, J. C. Ho, and H. C. Ku, Phys. Rev. B **47**, 12 178 (1993).

[7]R. J. Cava, B. Batlogg, J. J. Krajewski, L. W. Lupp, Jr., L. F. Schneemeyer, T. Siegrist, R. B. van Dover, P. Marsh, W. F. Peck, Jr., P. K. Galagher, S. H. Glarum, J. H. Marshall, R. C. Farrow, J. V. Waszczak, R. Hull, and P. Trevor, Nature **336**, 211 (1989).

[8]C. C. Lai, H. K. Fun, T. S. Lee, and H. C. Ku (unpublished).

[9]G. H. Hwang, J. H. Shieh, J. C. Ho, and H. C. Ku, Chin. J. Phys. **30**, 351 (1992); Physcia C **201**, 171 (1992).

[10]H. A. Mook, D. McK. Paul, B. C. Sales, L. A. Boatner, and L. Cusslen, Phys. Rev. B **38**, 12 008 (1988).

[11]D. McK. Paul, H. A. Mook, A. W. Hewat, B. C. Sales, L. A. Boaster, J. R. Thompson, and M. Mostoller, Phys. Rev. B **37**, 2341 (1988).

[12]Y. Y. Xue, P. H. Hor, Y. Y. Sun, Z. J. Huang, L. Gao, R. L. Meng, C. W. Chu, J. C. Ho, and C. Y. Wu, Physcia C **158**, 211 (1989).

[13]R. S. Fishman and S. H. Liu, Phys. Rev. B **40**, 11 028 (1989).

[14]J. A. Blanco, D. Gignoux, and D. Schmitt, Phys. Rev. B **43**, 13 145 (1991).