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Linear Temperature Term of Heat Capacity in Insulating and Superconducting La-Ba-Cu-O Systems

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The heat capacity of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ was investigated between 0.8 and 10 K. The linear temperature term γT of the heat capacity is absent in the antiferromagnetic-ordered region of $x \leq 0.02$. γ increases abruptly from $x = 0.02$ to $x = 0.04$ where the system is still insulating at low temperature, and seems to saturate at the order of $5 \text{ mJ/mol} \cdot \text{K}^2$ in the superconducting region of $x \geq 0.05$. The correlation between magnetic order and vanishing γT term and the existence of a finite γT term for Ba doping give support to the resonating-valence-bond picture.

74.70.Hk, 74.30.Ek, 75.50.Ee

The discovery of high- T_c superconductors^{1,2} has generated much interest in the basic properties of superconducting oxides and possible new mechanisms for high- T_c superconductivity.³ In the La_2CuO_4 system, the antiferromagnetic (AF) ordering has been confirmed by measurements of magnetic susceptibility,⁴ neutron scattering,⁵ muon spin relaxation,⁶ and nuclear quadrupole resonance (NQR).^{7,8} The magnetism is highly two dimensional in character and is expected to play a key role in the understanding of high- T_c superconductivity in the La-Ba-Cu-O and Y-Ba-Cu-O systems.⁹ The recent study of neutron scattering of La_2CuO_4 has revealed novel two-dimensional antiferromagnetic behavior.¹⁰ Anomalies of the nuclear relaxation rates in Ba-doped La_2CuO_4 have been found in the region between antiferromagnetic and superconducting states.¹¹

Anderson³ proposed that the undoped La_2CuO_4 system has a resonating valence-bond (RVB) ground state, and that high- T_c superconductivity develops as a result of doping of this new type of insulator. A striking consequence of the theory is that spin and charge degrees of freedom are decoupled in the RVB state. Although a large gap exists for charge excitations in the undoped materials, spin excitations behave like a gas of neutral massless fermions^{3,12,13} with a bandwidth of order J , the exchange energy of the problem. Therefore, down to the lowest temperature, a heat-capacity term linear in temperature, $C = \gamma T$, should be observed with $\gamma \sim J^{-1}$ on the order of $\frac{1}{2000} \text{ K}$.

In the case of doping, mean-field theory¹⁴⁻¹⁷ leads to a gap for spinons (the neutral spin excitations of the theory), but Anderson¹⁸ has argued that, because of the SU(2) symmetry of the spinons, the gaplessness of the spinon excitation spectrum persists within the superconducting and within the "normal" RVB phases, so that the γT term should be observed whenever the resonating singlet liquid is the doped or undoped ground state. The

fact that antiferromagnetism has been proved to exist experimentally⁴⁻⁸ in undoped and slightly doped $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (with $M = \text{Ba}$ or Sr) does not ruin the RVB picture, since the materials are 3D anisotropic layered materials. A small coupling $J_\perp \ll J$ between layers may counterbalance the energy difference between RVB and AF within each layer.

The sensitivity of the observed antiferromagnetic order to doping^{4,7,8} can be understood if RVB is more stable than AF in 2D, in which case our decreasing the exchange coupling of the 3D-AF state by decreasing the average spin per site may result in the stabilization of RVB again at small doping. Alternatively, one may speculate about the destruction of spinon density-wave ordering by changes of the pseudo-Fermi-surface nesting due to doping.⁹ Whatever the mechanism which allows a small hole concentration to destabilize AF, RVB predicts no γT term in the heat capacity of the AF phase. Such terms can only appear if magnetic ordering is destroyed, provided a pseudo-Fermi surface continues to exist in the doped materials.

γT terms have been found with values ranging from 0.5 to $1.8 \text{ mJ/mol} \cdot \text{K}^2$ in $\text{La}_2\text{CuO}_{4-y}$ ¹⁹ to values between 10 and $20 \text{ mJ/mol} \cdot \text{K}^2$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, whether superconducting²⁰ or insulating.²¹ Values of $5 \text{ mJ/mol} \cdot \text{K}^2$ are reported for $\text{La}_{2-x}\text{M}_x\text{O}_4$ with $x \approx 0.15$ and $M = \text{Sr}$ or Ba .²² The poor reproducibility of γ values has led many to believe that the T -linear terms were of extrinsic origin, and could be due to various inhomogeneities such as a high density of two-level systems (TLS)²³ which also lead to γT terms, of the order of $1 \text{ mJ/mol} \cdot \text{K}^2$, in the heat capacity of glasses, insulating or metallic disordered solids, and some ceramics.²⁴

In one case of simultaneous measurements of magnetic susceptibility and heat capacity on the same sample,^{4,25} a correlation seemed to exist between magnetic ordering and small γ ($< 1 \text{ mJ/mol} \cdot \text{K}^2$) on one hand, and super-

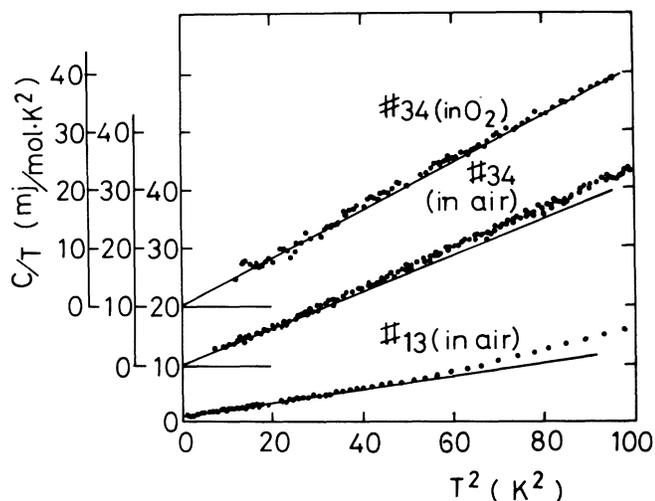


FIG. 1. Heat capacity plotted as C/T vs T^2 for three undoped La_2CuO_4 samples.

conducting state and large γ ($5 \text{ mJ/mol}\cdot\text{K}^2$), on the other hand. This seems to us to suggest that such terms are intrinsic, since magnetic ordering, and magnetic ordering alone, is capable of suppressing them, as mentioned above. Thus, we were prompted to study the possible correlation between γ and antiferromagnetism in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$.

Samples were prepared by our reacting the mixture of La_2O_3 , BaCO_3 , and CuO at 900°C in air for 12 h, sintering in pellet form at 1100°C , and annealing the pellet at 600°C for 12 h. Heat treatment for most samples was done in air atmosphere. A part of one sample (La_2CuO_4 No. 34) was annealed at 600°C for 200 h in oxygen atmosphere. The electrical resistance was measured by the standard four-wire method with ac and dc current of 0.1–10 mA. The magnetic susceptibility was also preliminarily measured. We confirmed the bulk superconductivity for $x \geq 0.05$. Heat-capacity measurements were made with the two different cryostats with a heat-pulse method. A ^3He cryostat with a calibrated carbon thermometer was used to measure down to 0.8 K. The heat capacity was also measured in another cryostat with a Ge thermometer down to 2 K and the results were compared with each other.

Figure 1 shows the heat capacities of three undoped La_2CuO_4 samples by plots of C/T vs T^2 . The heat capacities of La_2CuO_4 are somewhat different from sample to sample, and seem to depend on the sample quality. The temperature dependence of heat capacity is fitted by the relation $C = \gamma T + \beta T^3$ by the method of least squares in the low-temperature region. The heat capacity of No. 34 in O_2 atmosphere is well fitted from the highest temperature of 10 K. Here the T^3 term is from the phonon contributions in the Debye model. From the coefficients of the T^3 term in the low-temperature region, we deduce values of the Debye temperature of 240, 190, and 163 K

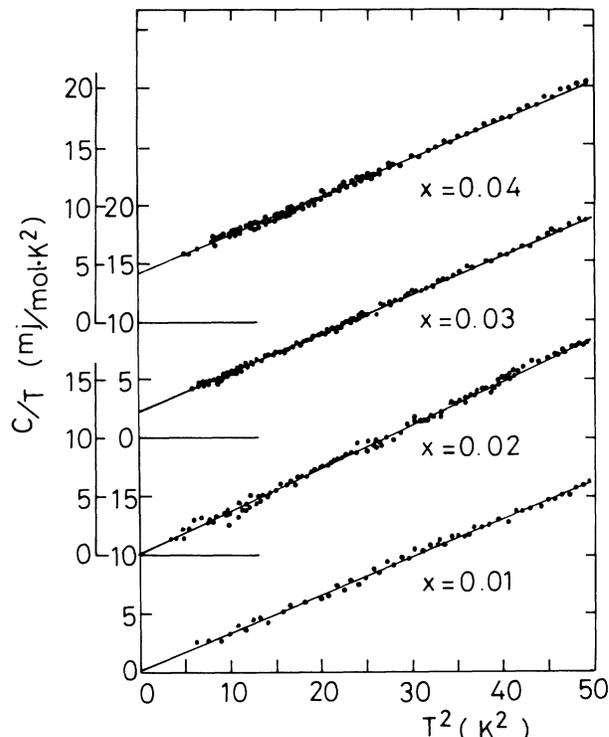


FIG. 2. Heat capacity plotted as C/T vs T^2 for nonsuperconducting $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. The solid lines are obtained by least-squares fitting below 7 K.

for samples No. 13, No. 34 (annealed in air), and No. 34 (annealed in oxygen), respectively. The magnitude of the T -linear term, γ , is obtained from extrapolation to $T=0$ by least-squares fitting. The γ values are at most $0.4 \text{ mJ/mol}\cdot\text{K}^2$ for sample No. 13 and between 0.0 and $0.5 \text{ mJ/mol}\cdot\text{K}^2$ for sample No. 34. Thus, γ in La_2CuO_4 is less than $0.5 \text{ mJ/mol}\cdot\text{K}^2$ within our experimental uncertainty.

Figure 2 shows the results of heat capacity of the Ba-doped samples by plots of C/T vs T^2 . The samples shown in this figure are still insulating as demonstrated by the measurements of electrical resistance.²⁶ The heat capacities are fitted by the relation $C = \gamma T + \beta T^3$ below 7 K. The Debye temperature is almost 180 K, independent of Ba concentration. γ is between 0 and $0.5 \text{ mJ/mol}\cdot\text{K}^2$ for $x < 0.02$ and increases rapidly up to 4–5 $\text{mJ/mol}\cdot\text{K}^2$ with increasing x . Figure 3 shows the C/T vs T^2 plots for superconducting samples. The heat capacity in the superconducting state is similar to that reported previously.^{22,25} γ for $x = 0.075$ is rather small compared to that for the other superconducting samples, but is still $2 \text{ mJ/mol}\cdot\text{K}^2$. The values of γ are shown in Fig. 4 as a function of Ba concentration together with the superconducting transition temperatures obtained by the electrical resistance measurement.^{8,11} The boundary of the antiferromagnetic phase in Fig. 4 is obtained by the NQR results^{8,11} for the same samples as the ones in the

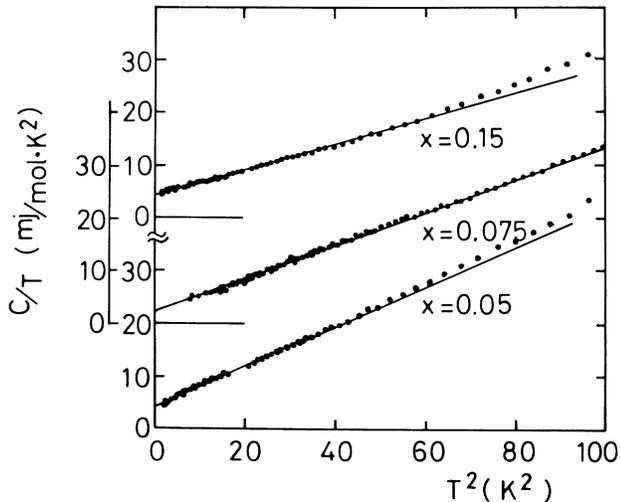


FIG. 3. Heat capacity plotted as C/T vs T^2 for superconducting $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. The solid lines are obtained by least-squares fitting in the lowest-temperature region.

present study.

The samples prepared by reacting in air atmosphere have few oxygen vacancies and many grain boundaries. Oxygen deficiencies are considered to increase with Ba doping for $x > 0.15$ but do not change much for small x .²⁷ Supposing such a defect structure could give rise to a tunneling T -linear term, γ would be expected to change linearly or smoothly with small doping of Ba. The large sample dependence of γ would also be expected. In the present samples of La_2CuO_4 with different preparation, the values of γ are scattered within at most $0.5 \text{ mJ/mol}\cdot\text{K}^2$ which is small compared to the order of $5 \text{ mJ/mol}\cdot\text{K}^2$ for $x > 0.02$. We see no reason for the contribution to γ due to TLS to increase abruptly from the concentration of $x = 0.02$. Therefore, it seems that the contribution to the heat capacity due to the TLS origin is not sizable for the La-Ba-Cu-O system and that the relatively large T -linear term for $x > 0.02$ arises from another origin.

It should be noted that γ is small or zero in the antiferromagnetic region and increases when the antiferromagnetic order disappears. Thus, our data seem to indicate a fairly strong correlation between magnetic ordering and vanishingly small (within experimental accuracy) γT term. This suggests an intrinsic origin for the γT term, when it is finite, and gives support to the RVB picture. The value for J which corresponds to $\gamma = 5 \text{ mJ/mol}\cdot\text{K}^2$ is $\approx 1000 \text{ K}$.

In the concentration range $0.01 \leq x \leq 0.05$, we have confirmed the anomalies of nuclear relaxation rates which are strongly peaked at a temperature T_c^* .¹¹ This range is an intermediate one between vanishing γ in AF ($x \leq 0.02$) and large γ in the superconducting state ($x \geq 0.05$). It seems that relaxation anomalies, clearly

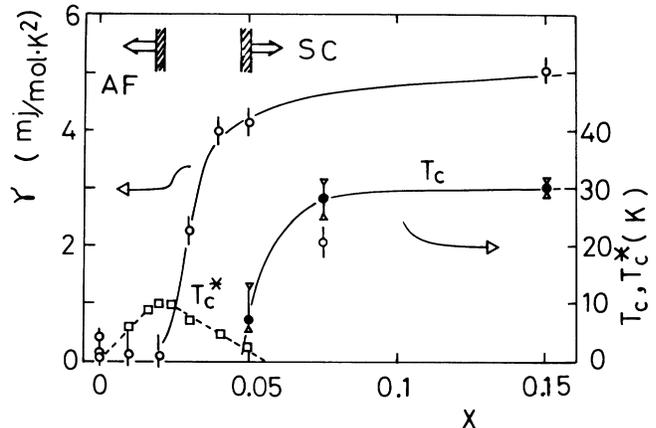


FIG. 4. Concentration dependence of the coefficients of the T -linear term of heat capacity, γ , of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. Superconducting transition temperatures, T_c , are also shown. Inverted triangles are from the onset of resistivity, filled circles are from midpoint, and triangles are from 10% above zero resistivity. The boundary of the antiferromagnetic phase is from the NQR results (Ref. 8). T_c^* (squares) is the temperature at which nuclear relaxation rates show the anomalies (Ref. 11).

associated with the fluctuations of spins, correspond to partial suppression of spinon density of states. Interestingly, such anomalous behavior of spin degrees of freedom at low temperature is not associated with anomalies in the heat capacity at T_c^* .

Evidence against the above interpretation of our data is the observation of antiferromagnetic ordering in the insulating compound $\text{YBa}_2\text{Cu}_3\text{O}_6$.²⁸ A large γ term ($15 \text{ mJ/mol}\cdot\text{K}^2$) has been observed in a compound with the same composition.²¹ This crucial point deserves careful experimental investigation. There is no evidence that the sample²¹ with large γ was antiferromagnetically ordered, and no evidence that the antiferromagnetically ordered sample²⁸ had a large γ term. Given the metallurgical uncertainties and the possible occurrence of large metastability of competing RVB and AF ground states, it is necessary to measure heat capacity and possible antiferromagnetism on the same sample. Only then shall we know if the properties of $\text{YBa}_2\text{Cu}_3\text{O}_6$ ruin the correlation which we have found between antiferromagnetism and vanishing γ in the insulating oxides. It is also necessary to check that different sample preparation procedures do not change the results qualitatively.

The extensive investigation of heat capacity associated with the NQR anomalies¹¹ will be given separately.

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