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# Approach to Curie-Weiss paramagnetism in the metallic perovskites $La_{1-x}Nd_xCuO_3$

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A procedure for the preparation of the starting oxides has allowed phase-pure synthesis of the rhombohedral, metallic perovskite system $La_{1-x}Nd_xCuO_3$ $(0 \leqslant x \leqslant 0.6)$ under 25 kbar oxygen pressure at 900–1000 °C. It was not possible to exceed the $x=0.6$ limit with 65 kbar at 1600 °C. Measurement of the $CuO_3$-sublattice contribution to the paramagnetic susceptibility $\chi_m(T)$ was obtained for samples of different $x$ by an appropriate subtraction of the $Nd^{3+}$-ion contribution as obtained from measurement of $\chi_m(T)$ for $NdAlO_3$. The data are qualitatively compatible with the Mott prediction for a mass-enhanced $\chi_m(T)$ of a half-filled band that approaches the Mott-Hubbard transition from the itinerant-electron side. However, a model of strong-correlation fluctuations in a mass-enhanced Fermi liquid provides an alternative description of the data that is supported by transport measurements and a remarkable sensitivity of the susceptibility to small structural changes.

Experimental investigation of the transition from Pauli to Curie-Weiss paramagnetism on narrowing a half-filled band toward the Mott-Hubbard transition has been frustrated by lattice instabilities that make difficult stabilization of phase-pure samples of a suitable single-valent system. We have overcome this problem with a high-pressure synthesis of stoichiometric, phase-pure $La_{1-x}Nd_xCuO_3$, $0 \leqslant x \leqslant 0.6$. This rhombohedral perovskite system is metallic; strong Cu-O covalent hybridization creates a narrow, half-filled $\sigma^*$ band of $e$-orbital parentage. Decreasing the size of the large lanthanide ion decreases the width $W_\sigma$ of the $\sigma^*$ band without changing the oxidation state of the $CuO_3$ array.

Landau mean-field theory provides a basic theoretical framework for describing the enhancement of the Pauli susceptibility of a metal by strong electron correlations. Stoner enhancement[1] is one solution applicable where the correlations are ferromagnetic. However, the Mott-Hubbard model is more appropriate for a half-filled band where antiferromagnetic correlations are dominant. Using the Gutzwiller variational approach, Brinkman and Rice[2] obtained a mass-enhanced susceptibility at $T=0$ K for a half-filled band that approaches the Mott-Hubbard transition from the metallic side. It was Mott[3] who first proposed the temperature dependence to be expected for a mass-enhanced susceptibility, introducing a transition at a temperature $T_d$ from a temperature-dependent susceptibility $\chi_m(T)$ for $T<T_d$ to an enhanced, nearly temperature-independent $\chi_m(T)$ for $T>T_d$. However, Mott was unable to find an experimental test-bed for his hypothesis. One of us[4] has pointed out that a linear dependence of $\chi_m^{-1}$ vs $T$ that gives an anomalously large Weiss constant $\theta$ and too large a Curie constant for a localized-electron $\mu_{\text{eff}}$ is characteristic of strongly correlated itinerant-electron magnetism, but lattice instabilities prevented a systematic study of the problem at that time.

The $LnCuO_3$ family of perovskites in which Ln is a trivalent lanthanide ions is an ideal candidate for the study of a narrow, half-filled $\sigma^*$ band on the $CuO_3$ array. An early measurement of $\chi_m(T)$ and conductivity for a nominal rhombohedral $LaCuO_3$ prepared under 65 kbar oxygen pressure and 900 °C by Demazeau *et al.*[5] indicated the compound is metallic with an enhanced Pauli paramagnetism and no long-range magnetic order or charge-density wave to lowest temperatures, but a number of questions concerning the synthesis temperature of their sample were raised by subsequent studies. Webb *et al.*[6] showed that rhombohedral $LaCuO_3$ is only stable above 1500 °C and 60 kbar pressure. Bringley *et al.*[7] discovered that stoichiometric $LaCuO_3$ may be tetragonal with cooperative rotations of $CuO_{6/2}$ octahedra about the [001] axis. The stoichiometric tetragonal phase converts to the rhombohedral structure, which has cooperative rotations of the $CuO_{6/2}$ octahedra about the [111] axis, only under 70 kbar oxygen pressure at high temperature.[8] Thermal analysis[9] has shown that the high-pressure rhombohedral phase is always fully oxygenated. A previous attempt[6] to make the perovskite system $La_{1-x}Nd_xCuO_3$ reported a solid-solution range $0 \leqslant x \leqslant 0.4$, but no further characterization of the samples was reported.

We have developed a synthetic procedure that has allowed stabilization of the $La_{1-x}Nd_xCuO_3$ rhombohedral phase over the solid-solution range $0 \leqslant x \leqslant 0.6$ in a belt apparatus at 25 kbar and 900–1000 °C. The starting oxides to be reacted under high oxygen pressure were separated from the oxygen source, $KClO_4$, by an yttria-stabilized $ZrO_2$ disk; this assembly was sealed in a gold capsule. Solid-state reaction between $La_{2-x}Nd_xCuO_4$ and CuO particles forms the $La_{1-x}Nd_xCuO_3$ product at the interface, and the product blocks the diffusion required for further reaction. Although coprecipitation of the oxides from solution gives an intimate mixing that allows preparation of the tetragonal $LaCuO_3$ phase at modest pressures, conversion to the rhombohedral phase of even the $LaCuO_3$ end member of the system $La_{1-x}Nd_xCuO_3$ requires 70 kbar pressure. Therefore, we prefired mixtures of $La_{1-x}Nd_xO_3+2CuO$ powders at 1100 °C for 20 h and ground the product in a shaking ball mill for 30 min. This procedure produced a very fine powder that contained a small amount of rhombohedral $LaCuO_3$. In order to reduce the volume loss of the mixture under high pressure in the belt apparatus, a Teflon cell was filled with the powder and pressed to 20 kbar at room temperature in a piston-cylinder system. With this prepressed pellet as the starting material for the application of high oxygen pressure in the

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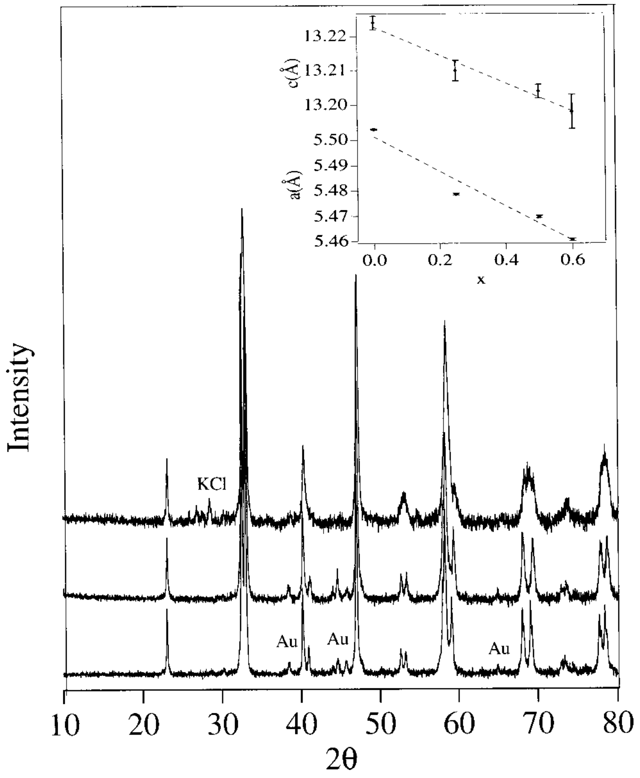

FIG. 1. Powder x-ray diffraction for $La_{1-x}Nd_xCuO_3$: bottom, $x=0$; middle, $x=0.25$; top, $x=0.5$. The inset shows the lattice parameter vs $x$.

belt apparatus, we were able to synthesize pure rhombohedral $La_{1-x}Nd_xCuO_3$ perovskites under 25 kbar pressure at 900–1000 °C over the compositional range $0 \leqslant x \leqslant 0.6$.

Figure 1 shows that as $x$ increases to 0.6, the x-ray-diffraction peak heights decrease relative to background, and the main KCl peak at $2\theta = 28.4°$ becomes visible. Beyond $x = 0.6$, the rhombohedral phase disappears; pressures to 65 kbar at 1600 °C were not able to change the phase boundary. We restricted ourselves to a study of the rhombohedral system $La_{1-x}Nd_xCuO_3$ in the range $0 \leqslant x \leqslant 0.6$, where the full oxygen stoichiometry is assured. For each composition, a single phase synthesized under the same pressure and temperature was found to be repeatedly reproducible. The gold color of $LaCuO_3$ darkened with increasing $x$. The inset of Fig. 1 shows the evolution with $x$ of the lattice parameters $a$ and $c$ referred to an hexagonal cell; they decrease linearly with $x$ in accordance with Végard's law for a solid solution.

Resistivity data were obtained with a four-probe method on rectangular samples cut from the central portion of the pellets from the high-pressure synthesis. The four corners of the rectangular samples were coated with Pt-Pd alloy before four thin cooper wires were attached with silver epoxy. The temperature dependence of the resistivity, $\rho(T)$, for compositions $x = 0.0$, 0.25, and 0.50 are shown in Fig. 2. The somewhat greater temperature dependence of the $x = 0.25$ sample is attributed to microcracks in the thin pellet samples. Significantly, all samples show a metallic temperature dependence with a low value of the resistivity (more than four orders of magnitude lower than that reported in Ref. 5). A low thermoelectric power in these samples[10] is consistent with a $\sigma^*$ band that is half-filled. These transport data verify that we are dealing with itinerant electrons in a half-filled band where antiferromagnetic electron correlations should be dominant.

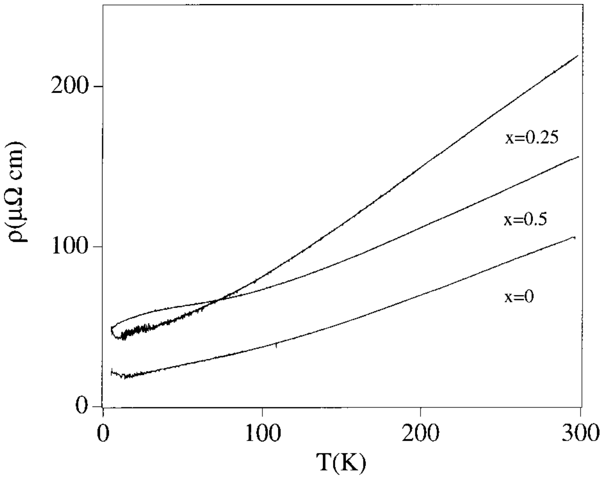

FIG. 2. Resistivity vs temperature for $La_{1-x}Nd_xCuO_3$.

Magnetic susceptibilities $\chi_m(T)$ were measured with a superconducting quantum interference device magnetometer (Quantum Design). The shape and orientation of the samples were made to minimize the demagnetization factor. For each composition, measurements were made on several samples obtained from different high-pressure syntheses. In order to subtract out the $Nd^{3+}$-ion contribution to $\chi_m(T)$, we also measured $\chi_m(T)$ of rhombohedral $NdAlO_3$. The $NdAlO_3$ sample was synthesized by standard solid-state reaction and shown to be single-phase by powder x-ray diffraction. Although the measured Curie constant $C = 1.615$ for $NdAlO_3$ is close to the free-ion value $C = 1.617$, nevertheless a large negative Weiss constant $\theta = 95$ K was obtained from the curve fitting. (Similar data were obtained with $NdGaO_3$.) Taking proper account of the constant $\theta$ is critical to the process of subtracting out the $Nd^{3+}$-ion contribution to the $La_{1-x}Nd_xCuO_3$ samples. A correction for the diamagnetism from the core electrons and the Landau contribution from the conduction electrons was not made as these corrections are two orders of magnitude lower than the measured paramagnetism of the $CuO_3$ array. However, the susceptibility of our $LaCuO_3$ sample is about four times lower than that reported by Demazeau *et al.*[5] We observed a higher susceptibility in samples synthesized at somewhat lower temperatures ($T < 900$ °C) that were either tetragonal or contained some tetragonal phase; a phase-pure sample is critical for achieving an intrinsic susceptibility of rhombohedral $LaCuO_3$.

Figure 3 shows the $\chi_m(T)$ curves for the $CuO_3$ array with different values of $x$; they all show a slope change near 200 K. Recovery of the change in slope of $\chi_m(T)$ for the $CuO_3$ array after subtracting the $Nd^{3+}$-ion contribution indicates that the subtraction has been done properly. The $\chi_m(T)$ curve for $LaCuO_3$, Fig. 3(a), is temperature-independent above 200 K, but it is enhanced by at least two orders of magnitude relative to a conventional Pauli paramagnetism. The temperature dependence of $\chi_m(T)$ below 200 K cannot be attributed to a Curie-Weiss paramagnetism from magnetic impurities. Given the high value of the temperature-independent susceptibility above 200 K, any magnetic-impurity paramagnetic contribution would only appear at ex-

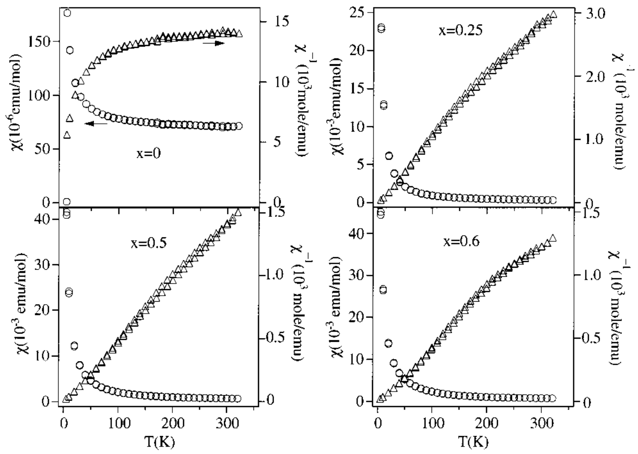

FIG. 3. Susceptibility $\chi_m(T)$ and $\chi_m^{-1}$ vs temperature for the $\mathrm{CuO_3}$ array of $\mathrm{La}_{1-x}\mathrm{Nd}_x\mathrm{CuO}_3$. The small difference below room temperature between the $\chi_m(T)$ data for field-cooled and zero-field-cooled runs in $H_a=5$ T appears to be due to a lateral displacement of the sample in the bore of the SQUID on thermal cycling.

tremely low temperatures. As the $\mathrm{Nd}^{3+}$-ion concentration $x$ increases, the $\mathrm{CuO_3}$ component of $\chi_m(T)$ increases and becomes temperature-dependent above 200 K. However, extrapolation of $\chi_m^{-1}$ to the temperature axis gives too high a Weiss constant $\theta$ to be meaningful, and the Curie constant is too large.

The susceptibility of the $\mathrm{CuO_3}$ array at 300 K, $\chi_{300}$, is shown in Fig. 4 to increase more than tenfold on going from $x=0$ to $x=0.6$. This extraordinary change indicates a narrowing of the width $W_\sigma$ of the $\sigma^*$ band of the $\mathrm{CuO_3}$ array at the approach to the Mott-Hubbard transition from the itinerant-electron side. With increasing $x$, $W_\sigma$ is narrowed by two factors: (1) perturbation of the periodic potential by two different $A$-site cations and (2) an increase in the mean bending angle $\phi$ of the $(180°-\phi)$ Cu-O-Cu bond angles to accommodate a decreasing geometric tolerance factor $t<1$. (The tolerance factor $t\equiv(A-O)/\sqrt{2}(\text{Cu-O})$ is a ratio of the equilibrium bond lengths, and $A=\mathrm{La}_{1-x}\mathrm{Nd}_x$.) However, the change $\Delta t=0.07$ over the range $0\leqslant x\leqslant 0.06$ is small, and a $W_\sigma\sim\cos\phi$ would vary little with $x$. Moreover, perturbation of the periodic potential by the two different lanthanide ions is relatively small since any magnetic-exchange interactions between $4f^n$ configurations and the $\sigma^*$-band electrons of a perovskite are small, as is attested to by the invariance with rare-earth ion of the superconductive critical temperatures $T_c$ of the copper-oxide superconductors. Therefore, the remarkable variation with $x$ in $\chi_{300}$ clearly marks the approach to some critical bandwidth for the transition from Pauli to Curie-Weiss paramagnetism.

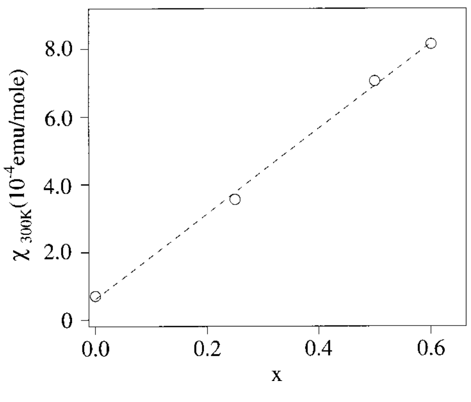

FIG. 4. Room-temperature susceptibility $\chi_{300}$ vs $x$ for the $\mathrm{CuO_3}$ array of $\mathrm{La}_{1-x}\mathrm{Nd}_x\mathrm{CuO}_3$.

At finite temperatures, thermodynamics introduces a factor $1/kT$ into the magnetic susceptibility. In the broad-band limit, the one-electron states having their moment $1\ \mu_B$ parallel to the applied field $H_a$ are stabilized relative to those of opposite spin by $2\mu_B H_a \ll W_b$, and thermal excitation of the states within $kT$ of the Fermi energy introduces another factor $kT$ to render the Pauli paramagnetism temperature-independent. In order to introduce a $T^{-1}$ temperature dependence, it is necessary to have states with a dispersion less than $kT$. The Stoner enhancement[1] by spin fluctuations associated with ferromagnetic interactions increases the susceptibility, but it does not introduce a flattening of the dispersion curve near the Fermi energy $\epsilon_F$. However, the Brinkman-Rice mass enhancement[2] is more relevant to our case of a half-filled band; it introduces a factor $[1-(U/U_c)^2]^{-1}$ in both effective mass and susceptibility that increases toward a singularity as the on-site correlation energy (Hubbard $U$) approaches the critical value $U_c$ for the Mott-Hubbard transition. In this model, renormalization of the electronic states introduces a flattening of the $\epsilon_{\mathbf{k}}$ vs $\mathbf{k}$ dispersion curve at $\epsilon_F$, and Mott[3] has pointed out that this flattening within an energy range $\Delta E\approx kT_d$ can introduce temperature-independent magnetic moments that give a *1/kT* contribution to $\chi_m(T)$ at lower temperatures $T<T_d$. At higher temperatures $T>T_d$, the Pauli paramagnetic contribution from the more dispersive electronic states dominates the susceptibility. This picture appears to describe well the $\chi_m(T)$ curve for $\mathrm{LaCuO_3}$ with a $T_d\approx 200$ K. However, it is not obvious from qualitative considerations to explain with this model the evolution of $\chi_m(T)$ with $x$, which shows little change in $T_d$ with an increase of over an order of magnitude in $\chi_{300}$.

An alternative model is suggested by the measurements[10] of the resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ of $\mathrm{La}_{1-x}\mathrm{Nd}_x\mathrm{CuO}_3$ under pressure. Photoemission spectroscopy (PES) for the single-valent, metallic system $\mathrm{Sr}_{1-x}\mathrm{Ca}_x\mathrm{VO}_3$ has shown the coexistence of strongly correlated electrons in states of a lower Hubbard band and a partially filled band of Fermi-liquid states; with increasing $x$, a monotonic transfer of spectral weight from the Fermi-liquid to the Mott-Hubbard band occurs.[11] This experiment provides direct evidence for a heterogeneous electronic model in which a singularity in the effective mass is avoided by the introduction of strong-correlation fluctuations as $U$ approaches $U_c$. We[12] have measured the resistivity $\rho(T)$ and the thermoelectric power $\alpha(T)$ of $\mathrm{CaVO_3}$ under pressure to confirm the implications of the PES data. Our data also showed that the transport properties provide indirect signatures for the heterogeneous model: (1) bad metallic behavior, (2) an anomalous $d|\alpha_{300}|/dP>0$, and (3) a suppression of the low-temperate phonon-drag component of $\alpha(T)$ that is partially restored by the application of pressure. Moreover, we have reported[10] that the system $\mathrm{La}_{1-x}\mathrm{Nd}_x\mathrm{CuO}_3$ exhibits these characteristic features of a heterogeneous model. In this model, the electrons of the lower Hubbard band impart a Curie-Weiss component to $\chi_m(T)$ and the Fermi-liquid states a mass-enhanced Pauli paramagnetic component. Moreover, heterogeneity is introduced by cooperative oxygen displacements that define the volume of a strong-correlation fluctuation as a region of longer mean Cu-O bond length.[10] It follows that the appearance of these fluctuations represents the onset of a strong electron coupling to the period of the cooperative oxygen vibrations, a period that may be more sensitive to the bond angle $\phi$ than is $W_\sigma$.

In summary, a new synthetic procedure has allowed us to synthesize under high oxygen pressure the rhombohedral perovskite $La_{1-x}Nd_xCuO_3$ with $0 \leqslant x \leqslant 0.6$; it is a high-pressure, metallic phase that is oxygen-stoichiometric and metastable over the temperature range $4 \leqslant T \leqslant 300$ K of our measurements. A continuous narrowing with increasing $x$ of a half-filled $\sigma^*$ band of $e$-orbital parentage—or lengthening of the period of cooperative oxygen vibrations that define strong-correlation functions—has allowed an investigation of the evolution from Pauli toward Curie-Weiss paramagnetism of the $CuO_3$ array obtained by an appropriate subtraction of the contribution from the $Nd^{3+}$ions. A remarkable more than tenfold increase in the room-temperature susceptibility over the range $0 \leqslant x \leqslant 0.6$ correlates with a small change $\Delta t = 0.07$ in the geometric tolerance factor and hence in the bandwidth $W_\sigma \sim \cos\phi$. It would appear that the period of the cooperative oxygen vibrations is at a critical crossover for trapping out of strong-correlation fluctuations. Although the temperature dependence of the magnetic susceptibility does not distinguish a homogeneous model with a strong mass enhancement from a heterogeneous model with strong-correlation functions, the transport properties and the sensitivity of $\chi_m(T)$ with $x$ favor a heterogeneous model. However, the data do differ sharply from the predictions of Edwards and Wohlfarth[13] for a system with Stoner enhancement and with those for a system with spin fluctuations put forward by Beal-Monod *et al.*[14]

The authors thank the NSF and TCSUH Houston for financial support.

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