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Oxygen isotope effects on the critical and Curie temperatures and Raman modes in the ferromagnetic superconductor $RuSr_2GdCu_2O_8$

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The effect of oxygen isotopic substitution on transition temperature T_c, the Curie temperature T_M, and Raman modes is investigated in the ferromagnetic superconductor $RuSr_2GdCu_2O_8$. A large positive oxygen isotope effect, $\alpha_{T_c}=1.6$, is observed in the zero resistance T_c value for as-prepared samples but a much smaller value $\alpha_{T_c}=0.12\pm0.04$ is found in the true T_c, where the superconductivity order parameter is established as signified by the rapid rise in $d\rho/dT$. Such a value is in keeping with other underdoped high-T_c superconductor cuprates. A rather small ($\alpha_{\mathrm{FM}}\approx0.02$) oxygen isotope effect is observed in the ferromagnetic transition. Raman modes for this material are identified by inspection of the spectra with progressive ^{18}O exchange, cation substitution, and structural considerations. [S0163-1829(99)51018-7]

The observation of an isotope effect in the transition temperature T_c was pivotal in inferring the phonon-mediated nature of the pairing interaction in classical BCS superconductors.[1] The isotope effect is quantified in terms of an exponent, $\alpha=-d\ln T_c/d\ln m$, where m is the isotopic mass. Ignoring coulomb effects, the BCS theory predicts a value of $\alpha=0.5$. This value was observed in Pb and Sn and deviations from it in transition metals have been accounted for by including the coulomb interaction.[2] In high-T_c superconductors (HTS's), the oxygen isotope effect is the easiest and most frequently studied. Because the potentially relevant phonon modes are dominated by oxygen motion a partial isotope effect may then be discussed: $\alpha_{\mathrm{O}}=-d\ln T_c/d\ln m_{\mathrm{O}}$. The value of α_{O} [and also α_{Cu} (Ref. 3)] shows a very strong dependence on hole concentration p for *underdoped* HTS cuprates,[4] which has been interpreted in terms of the role of the normal-state pseudogap in depressing T_c in spite of a rather p-independent superconducting energy gap Δ_0.[5] A more fundamental parameter then is $\alpha_\Delta=-d\ln\Delta_0/d\ln m_{\mathrm{O}}$. The strongly p-dependent value of α_{O} can be understood in terms of a more or less constant value of α_Δ and the rapidly growing pseudogap energy E_g in the underdoped region. The situation for overdoped samples is less clear and under current investigation. The nature of the isotope effect in HTS's places restrictions on any theory of the underlying mechanisms and is a central effect which must be accounted for.

The rutheno-cuprate $RuSr_2GdCu_2O_8$ possesses the remarkable property of superconductivity ($T_c\sim46\,\mathrm{K}$) microscopically coexisting with ferromagnetism ($T_M\sim132\,\mathrm{K}$).[6] Muon spin-relaxation measurements[6] reveal a spatially homogeneous ferromagnetic order parameter and a spontaneous field at the muon site of 720 G. Superconductivity (SC) survives because (i) the Ru moments probably align in the a-b plane so that there is no pair breaking in the CuO_2 layer,[6] and (ii) exchange coupling between the SC carriers and the Ru moments is weak.[7] Observation of the oxygen isotope effects in the superconducting (α_{T_c}) and ferromagnetic (α_{FM}) transitions and in the Raman spectra of $RuSr_2GdCu_2O_8$ are important steps towards characterizing this remarkable material and understanding the similarities and differences between this system and other HTS cuprates.

Here, using magnetometry, resistivity, ac susceptibility, and Raman spectroscopy, we assign Raman modes and examine the isotope effect in the superconducting and ferromagnetic transitions in $RuSr_2GdCu_2O_8$. Comparison is made with other HTS cuprates and with the recently-reported[8,9] large isotope effect in the ferromagnetic transition in the manganite $La_{1-x}Ca_xMnO_3$.

$RuSr_2GdCu_2O_8$ (Ru-1212) samples were synthesized by solid-state reaction of stoichiometric powders of RuO_2, $SrCO_3$, Gd_2O_3, and CuO. These were milled, calcined at 960 °C in air then reacted as pellets at 1010 °C in flowing nitrogen, then at 1050 °C, 1055 °C, 1060 °C, and 1065 °C in flowing oxygen. Each reaction was for 10 h and, between each, the samples were remilled and pelletized. After the final sinter the samples were furnace cooled to 200 °C in flowing oxygen. These have $T_c(R=0)=19\,\mathrm{K}$ and are referred to as samples A. A further set of samples was annealed for 7 days at 1060 °C in flowing oxygen, then slow cooled. For these, $T_c(R=0)$ moved up to 35 K. They are referred to as samples B. All samples were confirmed to be single phase by x-ray diffraction (XRD).

Initially it was anticipated that the Ru-1212 structure would be that of an oxygen-deficient tripled perovskite, i.e., similar to $GdBa_2Cu_3O_7$ (equivalently $CuBa_2GdCu_2O_7$) but with Ru replacing the chain Cu, and with both the intrachain and interchain oxygen sites occupied. However electron dif-

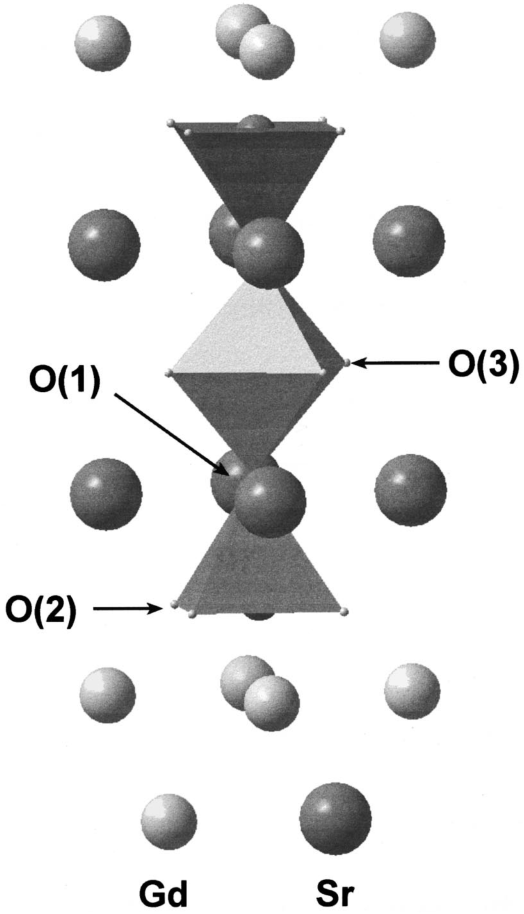

FIG. 1. The structure of $RuSr_2GdCu_2O_8$ showing the twist in the RuO_6 octahedra and the tilt in all polyhedra due to the displacement of the apical oxygen. The three oxygen sites are annotated.

fraction studies on samples B have shown the presence of weak superlattice reflections indicating a superlattice of $\sqrt{2}a\times\sqrt{2}b$ that is not present in samples A.[6] No superlattice is observed in the [001] direction. Synchrotron XRD Rietveld refinements[6] reveal two additional features: (i) a large off-site in-plane displacement (0.43 Å) of the oxygens in the RuO_2 layer resulting in a rotation of the RuO_6 octahedra, as is observed in $SrRuO_3$ (Ref. 10) and in the (Nb, Ta)-1212 compounds $(Nb,Ta)Sr_2RCu_2O_8$, where R is a rare-earth element;[11] and (ii) a smaller off-site in-plane displacement (0.12 Å) of the apical oxygen resulting in a tilting of both the CuO_5 square pyramids and the RuO_6 octahedra. The ordering of either of these rotations or tilts could result in the observed superlattices. The key feature from the point of view of Raman spectra is that the rotation of the RuO_6 octahedra lifts the inversion symmetry of the oxygens in the RuO_2 plane, thus rendering modes involving vibration of this oxygen Raman active. The structure is shown in Fig. 1 as a single polyhedral string which avoids the question of superstructural order which has yet to be determined.

Oxygen isotope exchange was achieved by parallel processing two pieces cut from the same sintered polycrystalline pellet. Sample spaces were evacuated and then charged with ^{16}O or ^{18}O at room temperature and the samples annealed in 1 atm at 810 °C. Several (up to seven) exchanges were carried out to achieve a high degree of exchange. Both samples were slow cooled to 200 °C, the original intention being to achieve full oxygenation. In fact, annealing samples at higher temperatures and in lower oxygen partial pressures has negligible effect on oxygen stoichiometry which remains fixed at 8 ± 0.02. Additionally, while such annealing influences the granularity and hence $T_c(R=0)$ value, it has no effect on the onset of superconductivity seen in the derivative $d\rho/dT$, which we will use to define the isotope effect. Hence, there is no influence on the measured isotope effect due to the negligible changes in oxygen stoichiometry. Moreover, T_c and mass remained the same for the normal-oxygen reference sample to within ±0.2 K and ±0.0001 g, respectively, on each exchange cycle and cooling.

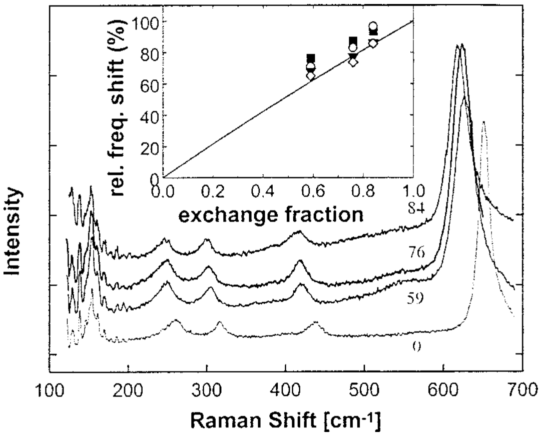

FIG. 2. Raman spectra for Ru-1212 samples with 0, 59%, 76%, and 84% ^{18}O exchange. The inset shows the relative frequency shifts of the oxygen modes. Solid line: expected harmonic dependence; squares 260 cm^{-1} mode; open circles 315 cm^{-1}; down triangle 440 cm^{-1}; open diamonds 650 cm^{-1}.

Temperature-dependent, zero-field-cooled susceptibility data were obtained using an EG&G 4500 vibrating sample magnetometer with an applied field of 5 Oe. Raman spectra were obtained using the 514.52 nm line of an Ar^+ laser and a Jobin-Yvon U1000 monochromator fitted with a CCD detector. The incident light was vertically polarized and the detected light unpolarized.

Raman spectra obtained for samples with pure ^{16}O, 59%, 76%, and 84% ^{18}O are shown in Fig. 2. The degree of exchange was determined by relative mass change after the ^{18}O exchange. The peak positions were determined by fitting Lorentzian line shapes in all cases, although some asymmetry is evident in the 260, 440, and 650 cm^{-1} modes. The mode at 153 cm^{-1} is assigned to purely c-axis Cu vibrations on the basis of this assignment in Y-124, Y-123, and Bi- and Tl-based cuprates at the same frequency.[12] Consistent with this interpretation this mode does not shift with oxygen isotope exchange. (The series of small features around the 153 cm^{-1} mode are experimental artifacts and do not correspond to cation modes.) The relative shifts of the remaining four higher frequency modes are collated in Table I. They are compared with the variation expected for harmonic mass dependence (solid line) in the inset to Fig. 2. All four modes are clearly associated with pure oxygen vibrations.

From the structure in Fig. 1 there are three distinct oxygen sites: the O(1) apical oxygens, O(2) oxygens in the CuO_2 plane, and O(3) oxygens in the RuO_2 plane. As noted, the

TABLE I. Raman mode positions and shifts with progressive ^{18}O exchange in $RuSr_2GdCu_2O_8$.

^{16}O	59% ^{18}O	% shift	76% ^{18}O	% shift	84% ^{18}O	% shift
153	153	nil	153	nil	153	nil
259.2	247.9	−4.36	246.3	−4.98	245.2	−5.35
316.6	303.8	−4.04	301.6	−4.74	299.0	−5.52
437.1	420.1	−3.89	417.8	−4.42	415.4	−4.94
651.5	627.3	−3.71	624.1	−4.21	619.8	−4.89

inversion symmetry of the O(3) oxygens in the RuO_2 layer is lifted by the octahedral rotations, and modes involving these oxygens should therefore be Raman active. By considering c-axis oxygen vibration at the remaining two sites, three modes are apparent: O(1), and in-phase and out-of-phase vibration of O(2). The most intense Raman peaks in cuprates are associated with c-axis vibrations so it seems reasonable, even without polarized spectra, to attribute these three modes to three of the four peaks. The 652 cm^{-1} peak is assigned to O(1) motion, as the highest-frequency oxygen modes in Y-123 and Y-124, and Tl-based cuprates are all associated with the apical oxygen.[12] The modes at 440 and 315 cm^{-1} are attributed to in- and out-of-phase motion of O(2) oxygens in the CuO_2 plane. Such modes have similar frequencies in Y-123, Y-124, Tl-1212, and Tl-2212 (in-phase mode only).[12] We believe that the remaining 260 cm^{-1} mode is associated with O(3) in the RuO_2 layer. To be more confident of these assignments and to identify the eigenvector of the O(3) mode, it is probably necessary to identify the structural basis of the observed superstructures. However, we note that there is a Raman-active phonon mode at 250 cm^{-1} in $SrRuO_3$ (Ref. 13) that corresponds to this O(3) assignment. More rigorous Raman investigation, including an identification of the lower frequency cation modes and temperature dependence of the spectrum[14] and the effect of cation substitution, is continuing.

Figure 3 shows the temperature-dependent ac susceptibility in the neighborhood of T_c for samples A and B as well as near T_M just for sample A. Unexchanged samples are shown by the solid curves and ^{18}O exchanged samples by the dashed curves. The degree of exchange was 84% for sample A while for sample B it was 82%. In the former case there is a very large reversible downward isotopic shift in T_c of 3.2 K in the ^{18}O exchanged sample giving $\alpha_{T_c} = +1.6$, while for sample B, T_c is shifted *up* by 0.59 K giving a negative isotope coefficient, $\alpha_O = -0.16$. The ferromagnetic transition in either case is only weakly affected with $\Delta T_M \approx 0.35$ K giving $\alpha_{FM} = -d \ln T_M / d \ln m_O \approx 0.02$. This represents a very small effect compared with the recently-reported isotope effect in T_M for $La_{1-x}Ca_xMnO_3$. Values of α_{FM} up to 0.85 have been observed by Zhao *et al.*[8] for x ranging from 0.1 to 0.2 while, for $x > 0.2$ where the ferromagnetic phase becomes metallic, Franck *et al.*[9] found that α_{FM} values fall abruptly to 0.38 then decrease rather more slowly towards 0.11 with increasing x. These effects have been interpreted in terms of strong coupling of the carriers to Jahn-Teller (JT) lattice distortions.[7] In $SrRuO_3$, where the JT effect is weak, no significant isotope effect was observed[7] as in the present case. The small shift in T_M reported here for Ru-1212 was confirmed in vibrating-sample-magnetometer (VSM) measurements on the same samples.

T_c values obtained from the ac susceptibility measurements on polycrystalline ceramics do not represent the onset temperature for a SC order parameter but rather the temperature at which screening currents flow across grain boundaries around the bulk sample. Nonetheless it is interesting that a large reproducible oxygen isotope effect is found for the establishment of phase coherence across grain boundaries. We obtain a clearer picture by examining the isotope dependence of the resistivity.

The inset to Fig. 4 shows the T dependence of the resis-

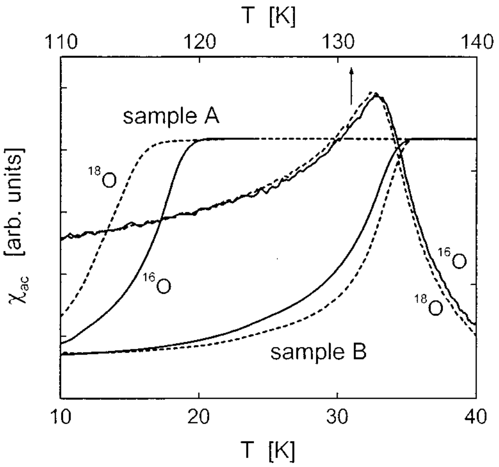

FIG. 3. ac susceptibility for unexchanged (solid curves) and 84% ^{18}O exchanged (dashed curves) Ru-1212 samples in the neighborhood of T_c and T_C: sample A (84% ^{18}O), sample B (82% ^{18}O).

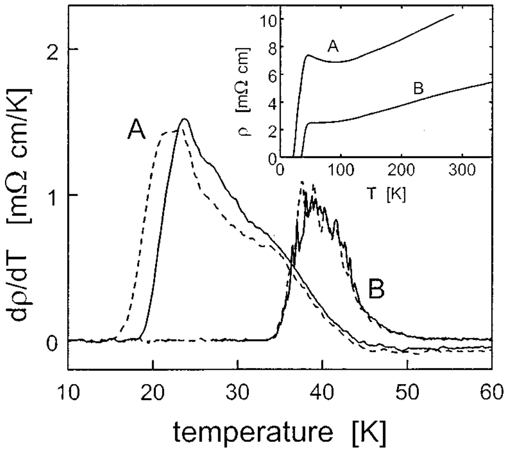

FIG. 4. The T dependence of the resistivity derivatives $d\rho/dT$ for the unexchanged (solid curve) and 84% exchanged (dashed curve) Ru-1212 samples A and B. Inset: resistivity of unexchanged samples A and B.

tivity for samples A and B. There is a small downward kink at T_M similar to that observed in $SrRuO_3$ and, at higher temperature (280 K), the knee in $\rho(T)$ is consistent with the opening of the pseudogap observed in other underdoped HTS cuprates.[15] This complements and confirms the thermopower data which indicates Ru-1212 is strongly underdoped with a hole concentration of $p\approx 0.07$.[6] The behavior of the resistivity at T_c is more easily seen in the derivative $d\rho/dT$ plotted in the main body of Fig. 4. At 46 K the derivative rises rapidly but does not fall to zero until the zero-field percolation temperature $T_c(R=0)\approx 19$ K in sample A or ≈35 K in sample B. A large isotopic shift in $T_c(R=0)$ is seen for sample A similar to that seen in the ac susceptibility and a similarly smaller value for sample B. In either case the onset temperature where $d\rho/dT$ rises rapidly occurs at the same temperature, 46 K. Heat capacity measurements[16] on these samples confirm the onset of bulk superconductivity at 46 K with a jump in $\gamma\equiv C_p/T$ of about 0.35 mJ/g at. K^2. While small, this value is again typical of similarly underdoped HTS cuprates.[17] The isotope shift in the leading edge of the resistive onset shown in Fig. 4 is 0.66 ± 0.2 K for sample A and 0.42 ± 0.2 K for sample B, giving coefficients $\alpha_{T_c}=0.14$ and 0.09, respectively. The difference between these values is probably not significant in our measurements and, because there is no reason to expect a difference, we conclude a value $\alpha_{T_c}=0.12\pm 0.04$. Such smaller values are more in keeping with other underdoped cuprates. For example, $YBa_2Cu_4O_8$, which is less underdoped, has $\alpha=0.076$.[5] We recall that our measurements are not influenced by oxygen stoichiometry variations which we have found to be negligible.

The usual approach in determining isotope shifted T_c values is to carry out magnetometry measurements of the intragranular diamagnetism. However in the present case the granularity is extremely fine, much smaller than the apparent grain size seen in scanning electron microscopy (0.5 μm for sample A and 5–10 μm for sample B). As a consequence the apparent volume susceptibility due to granular screening currents is less than 0.5% of the total at $T=0$. We are unable to determine with any reliability an isotopic shift in the onset of granular diamagnetism and therefore rely solely on the resistive onset in the present work. This granularity may in part be due to pair breaking from local misorientations of the spontaneous field at defects, twin boundaries, and subgrain boundaries, as well as the larger-scale grain boundaries.

As noted, a large isotope effect for underdoped cuprates can be discussed[5] in terms of the presence of the normal-state pseudogap which competes with superconductivity, strongly reducing T_c, the condensation energy, and the superfluid density. Quite generally, T_c is given by the temperature at which the pseudogap energy $E_g=\Delta(T)$. A variety of experiments indicate that, with progressive underdoping, $\Delta_0=\Delta(T=0)$ remains more or less constant while E_g rises rapidly towards Δ_0. As it does so T_c is reduced to zero. An isotope effect in T_c may arise from an isotope effect in Δ_0 or in E_g. NMR Knight shift studies indicate that, at least in the case of Y-124, there is no significant oxygen isotope effect in the pseudogap.[5] Consequently it would seem that the isotope effect is in the pairing interaction only. Either way, the model shows that α_{T_c} diverges as $E_g\rightarrow\Delta_0$, i.e., as $T_c\rightarrow 0$ with underdoping. The value of $\alpha_{T_c}=0.12\pm 0.04$ for Ru-1212 with $T_c=46$ K compared with, e.g., $\alpha_{T_c}=0.076$ for Y-124 with $T_c=81$ K, is entirely to be expected within this model.

In conclusion, we have assigned Raman modes for $RuSr_2GdCu_2O_8$ and observed a large positive oxygen isotope effect, $\alpha_{T_c}=1.6$, in the zero resistance T_c value for as-prepared samples. We observed a much smaller value $\alpha_{T_c}=0.12\pm 0.04$ in the true T_c where the SC order parameter is first established as signified by the rapid rise in $d\rho/dT$. Such a value is in keeping with other underdoped HTS cuprates. A small ($\alpha_{\mathrm{FM}}\approx 0.02$), if significant, oxygen isotope effect was observed in the ferromagnetic transition.

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