Sign reversal of the oxygen isotope effect on T_c in Sr$_2$RuO$_4$

Z. Q. Mao,[1,2] Y. Maeno,[1,2] Y. Mori,[1] S. Sakita,[3] S. Nimori,[3] and M. Udagawa[4]

[1]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*

[2]*Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation (CREST-JST),*
Kawaguchi, Saitama 332-0012, Japan

[3]*Venture Business Laboratory, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*

[4]*Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan*

We investigated the oxygen isotope effect (IE) on the transition temperature T_c in the spin-triplet superconductor Sr$_2$RuO$_4$ (with the intrinsic $T_{c0}=1.5$ K). A clear IE shift in T_c was observed. Moreover, we found that the IE coefficient alpha exhibits an unusual variation with T_c. For lower-T_c crystals containing impurities and defects, α is positive and increases with decreasing T_c; $\alpha(T_c)$ is described well by the universal behavior expected theoretically. However, for crystals with T_c approaching T_{c0}, α deviates from the universal $\alpha(T_c)$ and becomes negative. We discuss its possible mechanism on the basis of existing models.

I. INTRODUCTION

Sr$_2$RuO$_4$ is the first layered perovskite superconductor without copper.[1] On the basis of similarities of its Fermi-liquid parameters to ^{3}He and of the presence of the ferromagnetic relative compound SrRuO$_3$, Rice and Sigrist proposed the possibility of spin-triplet p-wave superconductivity.[2] Recent extensive experiments[3–5] provided considerable pieces of evidence for this expectation. An earlier theoretical study suggested that p-wave pairing in Sr$_2$RuO$_4$ is likely mediated by ferromagnetic (FM) fluctuation.[6] However, the uniform spin susceptibility[7] and the NMR measurement[8] revealed an enhanced paramagnetism. A recent study by inelastic neutron scattering[9] did not reveal any sizable FM fluctuations, but demonstrated the existence of incommensurate spin fluctuations predicted by the band-structure calculations.[10] In terms of these facts, Mazin and Singh discussed the possibility of a competition between p and d-wave superconductivities in Sr$_2$RuO$_4$.[10] Although the pairing mechanism is most likely due to spin fluctuations and electronic correlation, the roles of the enhanced paramagnetism and incommensurate spin fluctuations are not clear at present.

It is known that the isotope effect (IE) is an effective tool in a study of the pairing mechanism of superconductivity. An investigation by Raman scattering the on normal state of Sr$_2$RuO$_4$ revealed the existence of an anisotropic electron-phonon interaction.[11] To clarify how the p-wave pairing in Sr$_2$RuO$_4$ is influenced by the electron-phonon interaction, we investigated the oxygen IE on the transition temperature T_c in Sr$_2$RuO$_4$.

There is another important aspect to studying the oxygen IE of Sr$_2$RuO$_4$. We have shown that nonmagnetic impurity Al and defects in Sr$_2$RuO$_4$ result in a strong suppression of T_c.[12,13] The experimental ρ_0 (residual resistivity) vs T_c can be fitted very well using the modified Abriksov-Gor'kov (AG) equation

$$\ln(T_{c0}/T_c)=\psi(1/2+\gamma_s)-\psi(1/2), \tag{1}$$

where ψ is the digamma function, and $\gamma_s=\hbar/4\pi\tau T_c$ (τ is the scattering time, and is inversely proportional to ρ_0). T_{c0} is the value of T_c in the limit $\tau\to\infty$. The intrinsic T_{c0} deduced from this fitting is 1.5 K.

If we further assume $T_{c0}=T_{c0}(M)$ and $T_c=T_c(M)$ in Eq. (1), where M is the atomic mass of the relevant isotope, it is easy to obtain the relation between α_0 (the intrinsic IE coefficient in the ideal sample free of impurities and defects) and α (in the presence of impurities and defects) by taking the derivative of Eq. (1) and using the definition of the IE coefficient $\alpha=-d\ln T_c/d\ln M$ [this can also be expressed as $\alpha=-(M/\Delta M)(\Delta T_c/T_c)$ for $\Delta T_c\ll T_c$]. The derived relation[14] can be written as

$$\alpha/\alpha_0=[1-\psi'(\gamma_s+1/2)\gamma_s]^{-1}, \tag{2}$$

where ψ' is the derivative of ψ. This relation shows that the α increases with decreasing T_c in the presence of impurity.

In principle, the T_c dependence of α/α_0 in the presence of impurity, as shown by Eq. (2), is a universal one irrespective of the pairing mechanism, as long as the system satisfies the AG equation. Since the ρ_0-vs-T_c curve for Sr$_2$RuO$_4$ can be fitted with Eq. (1) very well, Sr$_2$RuO$_4$ is expected to be an ideal system to test this theoretical universal $\alpha(T_c)$ dependence. Therefore, we systematically investigated the T_c dependence of α in Sr$_2$RuO$_4$ using crystals with different T_c.

II. EXPERIMENTAL METHODS

The single crystals of Sr$_2$RuO$_4$ used in this study were grown by a floating-zone method. Most of the crystals with different T_c were obtained by an adjustment of the crystal growth conditions. For crystals with $T_c<1.0$ K grown at a faster speed, our previous study[13] showed that annealing under high temperature ($>1000\,$°C) can increase T_c strikingly. Hence it may have serious effect on the determination of T_c shift caused by oxygen isotope substitutions, since the ^{16}O $\to^{18}$O substitution has to be done by annealing at a temperature higher than 1000 °C. To avoid this annealing effect on T_c, we prepared some lower-T_c crystals by Al doping. Al-

though the distribution of Al in the crystal rod was not very homogeneous, we succeeded in obtaining two small pieces with a sharp transition and $T_c < 1.0$ K through careful selections. Annealing these samples at higher temperature did not show any substantial T_c enhancement.

To minimize the T_c variation by annealing, we first annealed the selected crystals with different T_c at 1050 °C for six days in flowing ^{16}O (step A). After this annealing, we measured T_c by ac susceptibility for each sample, as well as Raman spectra for some samples. Then using the same furnace, we performed ^{16}O$\rightarrow^{18}$O substitution (step B) for these annealed crystals. This substitution was conducted in a quartz tube, connected to a buffer volume at room temperature. The total volume of 2l was filled with ^{18}O to 0.95 bar. The samples were held at 1050 °C for six days. T_c and Raman spectra were measured again after this substitution. Furthermore, to evaluate the T_c shift caused by the oxygen isotope substitution more accurately, reverse ^{18}O$\rightarrow^{16}$O substitution (step C), as well as corresponding T_c and Raman-spectrum measurements were made after step B. The reverse substitution was done by annealing ^{18}O samples in the same condition as used in step A. For step B, we also tried using different annealing temperatures, but we found that the isotope shift in T_c is not observable if the annealing temperature is less than 1000 °C.

The ac susceptibility was measured by a mutual-inductance method. The precision of measured T_c is ± 1 mK. In Raman-scattering measurements, an Ar$^+$ laser with a wavelength of 514.5 nm was employed as the incident beam. Since Sr$_2$RuO$_4$ has a tetragonal lattice, four phonon modes are Raman active: two A_{1g} modes and two E_g modes. The A_{1g} modes appear for the incident and scattered polarization geometries of (a,a) or (c,c) and E_g for (c,a), where a and c denote $\langle 100 \rangle$ and $\langle 001 \rangle$ axes. The A_{1g} modes correspond to vibrations of Sr or apical oxygen along the c axis, and E_g modes to vibrations of Sr or apical oxygen along the a axis. The polarization geometry for all the measurements in this study is (c,c), in which the A_{1g} mode appears at ~ 202 cm^{-1} (P_1) for Sr vibrations and 545 cm^{-1} (P_2) for apical oxygen.[15] The measured ac surfaces were always finely polished with 1-μm diamond slurry after each annealing step.

III. EXPERIMENTAL RESULTS

Figure 1 shows the Raman spectra of one of the samples, $C82I3$. Curves A, B, and C correspond, respectively, to the results of measurements done after step A, B and C annealings on the identical sample. Clearly the Sr vibration mode P_1 does not show any frequency shift within the experimental precision with oxygen isotope substitution. In contrast, the apical oxygen vibration mode P_2 exhibits a remarkable isotope shift with ^{16}O$\rightarrow^{18}$O or ^{18}O$\rightarrow^{16}$O substitution, the relative magnitude of which is 15 cm^{-1}. Since the peak widths remain nearly the same, we conclude that the substitution is fairly uniform at least within the regions Raman spectrum can detect. It is worthwhile to mention that we also performed ^{17}O substitution for ^{16}O in Sr$_2$RuO$_4$ using the same annealing conditions as in step B, while preparing the
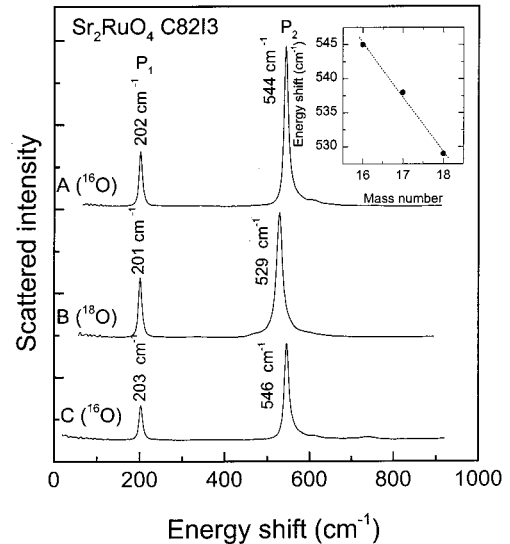

FIG. 1. Raman spectra of the sample Sr$_2$RuO$_4$ measured after step A, B, and C annealings. The inset shows the dependence of the phonon vibration frequency of the apical oxygen on the isotope mass.

samples for NMR measurements.[3] The phonon frequency of P_2 in the ^{17}O samples was 538 cm^{-1}. We summarized the P_2 frequency data of ^{16}O, ^{17}O, and ^{18}O samples in the inset of Fig. 1. For these three points, the frequency of P_2 shows a fairly good harmonic mass dependence. It can be deduced that if the exchange ratio of ^{16}O$\rightarrow^{18}$O is 100%, the frequency of P_2 is 514 cm^{-1} in the ^{18}O samples, which is 15 cm^{-1} smaller than the measured value. This suggests that the probable exchange ratio is ~ 50%. This exchange ratio occurred in most of the samples we studied. Higher exchange ratio of ~ 80% was detected only in four samples. The exchange ratio discussed here is for the apical oxygen, since the P_2 reflects apical oxygen vibration. For the in-plane oxygen atoms which are non-Raman-active, the intensities of ^{17}O NMR peaks indicated that they are equally substituted as apical oxygen.[8] Thus we deduce that the in-plane exchange ratio of ^{16}O$\rightarrow^{18}$O is also ~ 50%.

To examine whether the oxygen isotope penetrates throughout the whole sample, we measured the dependence of Raman spectra on the depth polished at the measured surface. We found that ^{18}O does not penetrate deep into the crystals, because we did not detect any frequency shift after a surface layer of thickness 200 μm was removed. Nevertheless, the ^{18}O penetration depth is estimated to be greater than 100 μm. This is sufficient for the ac susceptibility measurement, since it only detects within an order of magnitude greater than the London penetration depth ($\lambda_L \sim 4$ and 0.2 μm along the c-axis and in-plane directions, respectively). Within the regions detected by ac susceptibility, the ^{18}O isotope distribution should be homogeneous, since the observed transition width in ac susceptibility did not broaden by ^{18}O substitution, as we will show below.

Even with 50% substitution of ^{18}O for ^{16}O on the surface layer, a clear IE on T_c was observed for crystals with differ-
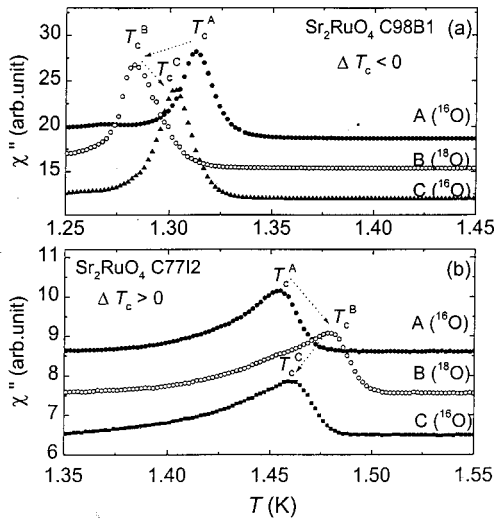
FIG. 2. Temperature dependence of the imaginary part of the ac susceptibility (χ'') for the samples (a) $C98B1$ and (b) $C77I2$, measured after step A, B, and C annealings.

FIG. 3. The dependence of the isotope coefficient α on the reduced superconducting critical temperature T_c/T_{c0} in Sr_2RuO_4. The dashed line is the universal $\alpha(T_c)$ dependence given by Eq. (2), with $\alpha_0 = 0.18$. The data points with $T_c/T_{c0} = 0.476$ and 0.683 are obtained with the Al-doped samples.

ent T_c. Figures 2(a) and 2(b) show the χ'' (imaginary part of the ac susceptibility) data of two typical samples ($C98B1$ and $C77I2$) measured after each annealing step. We define T_c as the peak temperature of χ''. Although this definition somewhat underestimates the transition temperature, we use it for the sake of better precision. We use T_c^A, T_c^B, and T_c^C to denote the measured T_c after step A, B and C annealings. $\Delta T_c = (\Delta T_{c1} + \Delta T_{c2})/2$ ($\Delta T_{c1} = T_c^B - T_c^A$, $\Delta T_{c2} = T_c^B - T_c^C$) is defined as the averaged isotope shift in T_c. In an ideal case, T_c^A should be identical to T_c^C. But what we observed experimentally for all the samples we studied, as shown in Fig. 2, is $T_c^A \neq T_c^C$. The slight reduction in T_c (like $C98B1$) may be mainly attributable to the contamination from the quartz tube used for the furnace, while the slight increase ($C77I2$) in T_c could result from the dominant annealing effect on T_c, which is not eliminated completely in step A annealing. From Fig. 2, it can be seen that ΔT_c is negative for the sample $C98B1$ but positive for $C77I2$. Positive ΔT_c means an inverse IE (negative α).

To obtain a systematic dependence of ΔT_c on T_c, we investigated many samples with T_c ranging from 0.6 to 1.5 K. For the case of $T_c < 1.0$ K, the Al-doped samples with a sharper transition were used. All results are summarized in Fig. 3, where ΔT_c is transformed into α using the definition $\alpha = -(M/\Delta M)(\Delta T_c/T_c)$ (we assume $\Delta M/M = 0.5(18 - 16)/16 = 0.062$ for the 50% exchange, and 0.1 for the 80% exchange). Obviously α exhibits an unusual variation with T_c: it is positive and increases with decreasing T_c for lower-T_c crystals containing impurities or defects, but becomes negative for T_c approaching T_{c0}. For the behavior of negative α with T_c close to T_{c0}, we have confirmed this very carefully. The different symbols in Fig. 3 represent the data obtained by independent annealing runs. The error bars in Fig. 3 represent the difference between T_c^A and T_c^C, which is caused by contamination and/or annealing effects. H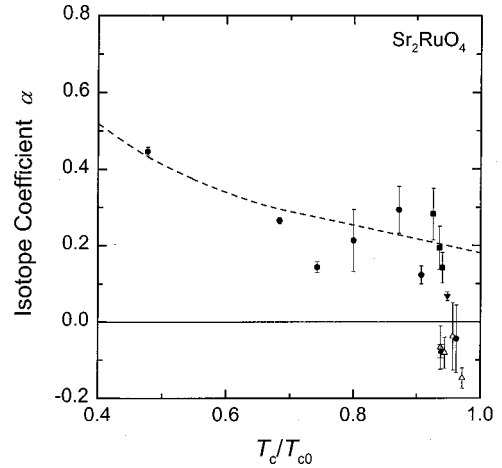ere it should be emphasized that such an unusual T_c dependence of α is intrinsic to Sr_2RuO_4, rather than due to contamination and/or annealing effect, since the change of α with T_c is significant compared with the magnitude of the error bars.

IV. DISCUSSIONS

It is clear that the variation of α with T_c in Fig. 3 cannot be fitted well with Eq. (2) in a whole range. Nevertheless, if we omit the data above $T_c/T_{c0} = 0.93$, the rest of the data can be fitted well with Eq. (2) by assuming $\alpha_0 = 0.18$ (see the dashed line in Fig. 3). This most probably indicates that the pair-breaking effect by impurities or defects is prominently responsible for the α enhancement with decreasing T_c for $T_c/T_{c0} < 0.93$. We have made two assumptions to derive the universality. The first assumption, the applicability of Eq. (1), seems to be satisfied even when T_c actually exceeds $0.93T_{c0}$.[13] We therefore question the validity of the other assumption, the invariance of the function $T_c = T_c(M)$, in order to explain the deviation from the universality. Below we will discuss an additional mechanism which leads to negative IE when T_c actually approaches T_{c0}.

In the framework of Bardeen-Cooper-Schrieffer theory in the weak-coupling limit,[16] the electron-electron pairing is mediated by phonons, and α is equal to 0.5 if Coulomb repulsion is neglected, i.e., $\mu^* = 0$. Thus $\alpha = 0.5$ is often regarded as a measure of the phonon contribution to the pairing mechanism. In reality, several factors can alter α,[17] for instance, the pair-breaking effect by impurity as we discussed above. For most of the nontransition elements such as Hg, Tl, and Cd, α is indeed almost equal to 0.5, while for transition elements such as Mo, Os and Ru, α is much less than 0.5 owing to nonzero μ^* (for a review, see Ref. 17). Negative α was actually observed as well, previously in PdH(D) ($\alpha = -0.25$) (Ref. 18) and U($\alpha = -2$),[19] and recently in some high-T_c superconductors.[20,21]

Several possible mechanisms have been proposed to un-

derstand these inverse IE. They may be summarized as (a) a large value of μ^*,[22] (b) the van Hove singularity in the electronic density of states,[23] and (c) an anharmonic phonon effect.[24] Although all three models were originally based on electron-phonon mechanism, they can be extended to a more general case as long as the interaction parameters depend on isotopic mass. For Sr_2RuO_4, although its pairing is likely mediated by spin fluctuation, an IE is expected if we assume the orbital motion of electrons affected by phonons is coupled with spin. In fact, a substantial spin-orbital coupling in Sr_2RuO_4 has been supported by a recent observation on Josephson coupling between a conventional superconductor In and Sr_2RuO_4.[25] From this point of view, the above models are still applicable to examine the negative IE in Sr_2RuO_4. For model (a), $\alpha < 0$ is possible for a large μ^*, but substantially negative α is unlikely. For (b), if the pairing is the electronic origin in the presence of a van Hove singularity near ε_F, the cutoff energy may be limited by $\omega_0 = \varepsilon_F - \varepsilon_{vH}$ (ε_{vH} is the energy of the van Hove singularity), instead of ω_D (the characteristic phonon frequency) and no isotope shift in T_c is expected. In this scenario, α can become negative by taking the Coulomb repulsion into account.[23] The anharmonic phonon effect (c) was previously proposed with PdH(D)[18] and recently used to explain the doping dependence of α in high-T_c superconductors.[24,26,27] Crudely speaking, some quantities that are independent of ionic masses in the harmonic approximation can become mass dependent in the presence of anharmonicity, and this leads to an anomalous α value of both above 0.5 and below 0.

Among these three models, (a) does not seem to hold since $\alpha = -0.15$, which is substantially negative. For model (b), the van Hove singularity associated with the γ Fermi surface[10] may play an important role, but it alone cannot explain why $\alpha(T_c)$ deviates from the universality only for high-T_c samples. The anharmonic phonon effect, model (c), appears to be more relevant to the sign reversal of the IE in Sr_2RuO_4, since its phonon dispersion, revealed by neutron scattering,[28] shows a strongly anharmonic feature, i.e., a softening of the rotation mode of RuO_6 octahedra. The softening of the phonons competes with the pair-breaking effect by impurity or defects, and becomes dominant in impurity-free samples with $T_c \approx 1.5\,K$, thus accounting for the unusual $\alpha(T_c)$ dependence shown in Fig. 3. To clarify this effect, further investigation of the phonon dispersion on the ^{18}O substituted samples by neutron scattering would be useful.

V. CONCLUSION

In conclusion, we observe a clear oxygen isotope effect in Sr_2RuO_4. α shows a systematic change with T_c. α is positive and grows with decreasing T_c for $T_c/T_{c0} < 0.93$, but becomes negative with $T_c/T_{c0} > 0.93$. The intrinsic α_0 is negative: $\alpha_0 = -0.15 \pm 0.03$. This unusual $\alpha(T_c)$ dependence may be explained by taking both pair-breaking and anharmonic phonon effects into account.

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