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

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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, $\alpha$ 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 $T_{c0}$, $\alpha$ 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$_4$. 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 $T_c$. The experimental $\rho_0$ (residual resistivity) vs $T_c$ can be fitted very well using the modified Abrikosov-Gor’kov (AG) equation

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

where $\psi$ is the digamma function, and $\gamma_s = h/4\pi \tau T_c$ ($\tau$ is the scattering time, and is inversely proportional to $\rho_0$). $T_{c0}$ 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 $T_c = T_{c0}(M)$ in Eq. (1), where $M$ is the atomic mass of the relevant isotope, it is easy to obtain the relation between $\alpha_0$ (the intrinsic IE coefficient in the ideal sample free of impurities and defects) and $\alpha$ (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$^{12}$ can be written as

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

where $\psi'$ is the derivative of $\psi$. This relation shows that the $\alpha$ increases with decreasing $T_c$ in the presence of impurity.

In principle, the $T_c$ dependence of $\alpha/\alpha_0$ 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 $\rho_0$ 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 $\alpha$ 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 $^{18}$O $\to$ $^{16}$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 $T_c < 1.0 \text{ K}$ 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 $\text{°C}$ for six days in flowing $^{18}\text{O}$ (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 $^{16}\text{O} \rightarrow ^{18}\text{O}$ 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 21 was filled with $^{18}\text{O}$ to 0.95 bar. The samples were held at 1050 $\text{°C}$ 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 $^{18}\text{O} \rightarrow ^{16}\text{O}$ 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 $^{18}\text{O}$ 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 $\text{°C}$.

The ac susceptibility was measured by a mutual-inductance method. The precision of measured $T_c$ is $\pm 1 \text{ mK}$. In Raman-scattering measurements, an $\text{Ar}^+$ 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 correspond 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 $\sim 202 \text{cm}^{-1}$ ($P_1$) for Sr vibrations and 545 cm$^{-1}$ ($P_2$) for apical oxygen.$^{15}$ The measured ac surfaces were always finely polished with 1-$\mu\text{m}$ diamond slurry after each annealing step.

III. EXPERIMENTAL RESULTS

Figure 1 shows the Raman spectra of one of the samples, C$82\text{I}3$. 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 $^{16}\text{O} \rightarrow ^{18}\text{O}$ or $^{18}\text{O} \rightarrow ^{16}\text{O}$ substitution, the relative magnitude of which is $15 \text{ cm}^{-1}$. 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 $^{17}\text{O}$ substitution for $^{16}\text{O}$ in Sr$_2$RuO$_4$ using the same annealing conditions as in step B, while preparing the samples for NMR measurements. The phonon frequency of $P_2$ in the $^{17}\text{O}$ samples was 538 cm$^{-1}$. We summarized the $P_2$ frequency data of $^{16}\text{O}$, $^{17}\text{O}$, and $^{18}\text{O}$ 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 $^{16}\text{O} \rightarrow ^{18}\text{O}$ is 100%, the frequency of $P_2$ is 514 cm$^{-1}$ in the $^{18}\text{O}$ samples, which is 15 cm$^{-1}$ smaller than the measured value. This suggests that the probable exchange ratio is $\sim 50\%$. This exchange ratio occurred in most of the samples we studied. Higher exchange ratio of $\sim 80\%$ 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 $^{17}\text{O}$ NMR peaks indicated that they are equally substituted as apical oxygen. Thus we deduce that the in-plane exchange ratio of $^{16}\text{O} \rightarrow ^{18}\text{O}$ is also $\sim 50\%$.

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 $^{18}\text{O}$ does not penetrate deep into the crystals, because we did not detect any frequency shift after a surface layer of thickness 200 $\mu\text{m}$ was removed. Nevertheless, the $^{18}\text{O}$ penetration depth is estimated to be greater than 100 $\mu\text{m}$. 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 $\mu\text{m}$ along the $c$-axis and in-plane directions, respectively). Within the regions detected by ac susceptibility, the $^{18}\text{O}$ isotope distribution should be homogeneous, since the observed transition width in ac susceptibility did not broaden by $^{18}\text{O}$ substitution, as we will show below.

Even with 50% substitution of $^{18}\text{O}$ for $^{16}\text{O}$ on the surface layer, a clear IE on $T_c$ was observed for crystals with differ-
From Fig. 2, it can be seen that which is not eliminated completely in step an inverse IE

The ac susceptibility defined as the averaged isotope shift in for the case of in Fig. 3 represent the difference between data obtained by independent annealing runs. The error bars very carefully. The different symbols in Fig. 3 represent the mentally for all the samples we studied, as shown in Fig. 2, a sample could result from the dominant annealing effect on a. Obviously a negative IE when a approaching zero. For the behavior of negative a with Tc close to Tc,0, 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 TcA and TcC, which is caused by contamination and/or annealing effects. Here it should be emphasized that such an unusual Tc dependence of a is intrinsic to Sr2RuO4, rather than due to contamination and/or annealing effect, since the change of a with Tc is significant compared with the magnitude of the error bars.

IV. DISCUSSIONS

It is clear that the variation of a with Tc in Fig. 3 cannot be fitted well with Eq. (2) in a whole range. Nevertheless, if we omit the data above Tc/Tc,0 = 0.93, the rest of the data can be fitted well with Eq. (2) by assuming a0 = 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 a enhancement with decreasing Tc for Tc/Tc,0 < 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 Tc actually exceeds 0.93Tc,0.13 We therefore question the validity of the other assumption, the invariance of the function Tc = Tc(M), in order to explain the deviation from the universality. Below we will discuss an additional mechanism which leads to negative IE when Tc actually approaches Tc,0.

In the framework of Bardeen-Cooper-Schrieffer theory in the weak-coupling limit,16 the electron-electron pairing is mediated by phonons, and a is equal to 0.5 if Coulomb repulsion is neglected, i.e., μ* = 0. Thus a = 0.5 is often regarded as a measure of the phonon contribution to the pairing mechanism. In reality, several factors can alter a,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, a is indeed almost equal to 0.5, while for transition elements such as Mo, Os and Ru, a is much less than 0.5 owing to nonzero μ* (for a review, see Ref. 17). Negative a was actually observed as well, previously in PdH(D) (a = −0.25) (Ref. 18) and U(a = −2),19 and recently in some high-Tc superconductors.20,21

Several possible mechanisms have been proposed to un-
Understand these inverse IE. They may be summarized as (a) a large value of $\mu^*$,\(^\text{22}\) (b) the van Hove singularity in the electronic density of states,\(^\text{23}\) and (c) an anharmonic phonon effect.\(^\text{24}\) 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$_2$RuO$_4$, 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$_2$RuO$_4$ has been supported by a recent observation on Josephson coupling between a conventional superconductor and Sr$_2$RuO$_4$.\(^\text{25}\) From this point of view, the above models are still applicable to examine the negative IE in Sr$_2$RuO$_4$. For model (a), $a<0$ is possible for a large $\mu^*$, but substantially negative $a$ is unlikely. For (b), if the pairing is the electronic origin in the presence of a van Hove singularity near $e_F$, the cutoff energy may be limited by $\omega_D = e_F - e_{\text{vH}}$ ($e_{\text{vH}}$ is the energy of the van Hove singularity), instead of $\omega_D$ (the characteristic phonon frequency) and no isotope shift in $T_c$ is expected. In this scenario, $a$ can become negative by taking the Coulomb repulsion into account.\(^\text{25}\) The anharmonic phonon effect (c) was previously proposed with PDH(D)\(^\text{18}\) and recently used to explain the doping dependence of $a$ in high-$T_c$ superconductors.\(^\text{24,26,27}\) 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 $a$ of both above 0.5 and below 0.

Among these three models, (a) does not seem to hold since $a = -0.15$, which is substantially negative. For model (b), the van Hove singularity associated with the $d$ Fermi surface may play an important role, but it alone cannot explain why $a(T_c)$ 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$_2$RuO$_4$, both since its phonon dispersion, revealed by neutron scattering,\(^\text{28}\) 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 $a(T_c)$ 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$_2$RuO$_4$. $\alpha$ shows a systematic change with $T_c$. $\alpha$ is positive and grows with decreasing $T_c$ for $T_c/T_c^{0}$$<$$0.93$, but becomes negative with $T_c/T_c^{0}$$>$$0.93$. The intrinsic $\alpha_0$ is negative: $\alpha_0 = -0.15 \pm 0.03$. This unusual $a(T_c)$ dependence may be explained by taking both pair-breaking and anharmonic phonon effects into account.

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