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Comment on “Isotope effect in high- T_c superconductors”A. S. Alexandrov¹ and G. M. Zhao²¹*Department of Physics, Loughborough University, Loughborough LE11 3TU, United Kingdom*²*Department of Physics and Astronomy, California State University, Los Angeles, California 90032, USA*

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We show that the recent reinterpretation of oxygen-isotope effects in cuprate superconductors by Harshman *et al.* [Phys. Rev. B **77**, 024523 (2008)] is mathematically and physically incorrect violating the Anderson theorem and the Coulomb law.

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The doping-dependent oxygen-isotope effect (OIE), α , on the critical superconducting temperature T_c (for recent reviews see Ref. 1) and the substantial OIE on the carrier mass,² α_m^* , provide direct evidence for a significant electron-phonon interaction (EPI) in cuprate superconductors. High-resolution angle-resolved photoemission spectroscopy (ARPES) (Ref. 3) provides further evidence for the strong EPI (Ref. 4) apparently with *c*-axis-polarized optical phonons. These results along with optical⁵⁻⁷ and neutron-scattering^{8,9} spectroscopies unambiguously show that lattice vibrations play a significant but unconventional role in high-temperature superconductivity. The interpretation of the optical spectra of high- T_c materials as due to many-polaron absorption¹⁰ strengthens the view¹¹ that the Fröhlich EPI is important in those structures. Operating together with a short-range deformation potential and molecular-type (e.g., Jahn-Teller¹²) EPIs, the Fröhlich EPI can readily overcome the Coulomb repulsion at a short distance of about the lattice constant for electrons to form real-space intersite bipolarons or Cooper pairs depending on doping.¹³

Despite all these remarkable and well-done experiments that lead to the consistent conclusion about the important role of EPI in high-temperature superconductors, Harshman *et al.*¹⁴ have recently claimed that the observed large OIE is caused by a disorder-induced pair breaking rather than by strong electron-phonon coupling and/or polaronic effects. Based on their reinterpretation of OIE, they conclude that EPI is allegedly too weak to explain high T_c in all the high- T_c materials. Here we show that the reinterpretation of OIE (Ref. 14) is internally inconsistent being at odds with a couple of fundamental physical laws. More specifically we show that the reinterpretation stems from a mathematically incorrect formalism.

Given the added claim that the pairing symmetry is nodeless *s* wave, the authors in Ref. 14 have assumed that the variation in T_c with doping is determined by the “universal” relation

$$\ln(T_{c0}/T_c) = a[\psi(1/2 + 1/T_c\tau) - \psi(1/2)] \quad (1)$$

which was originally derived by Abrikosov and Gor'kov¹⁵ with the coefficient $a=1$ to describe the pair-breaking effect by magnetic impurities in conventional *s*-wave BCS superconductors. Here T_{c0} is the critical temperature of optimally doped compounds in the absence of pair breaking, $\psi(x)$ is the

digamma function and $\tau=4\pi\tau_{tr}$ is proportional to the transport relaxation time, τ_{tr} , due to impurities, which are thought to be responsible for the suppression of T_{c0} (we take $\hbar=k_B=1$ here and further). Since *nonmagnetic* disorder in cuprate superconductors also often depresses T_{c0} , Harshman *et al.*¹⁴ have erroneously relaxed the requirement of magnetic impurities applying Eq. (1) to nonmagnetic impurities with the same coefficient $a=1$.

In fact, the coefficient a in Eq. (1) strongly depends on the pairing symmetry¹⁶ as analyzed in detail by Fehrenbacher and Norman.¹⁷ For nonmagnetic impurities $a=1$ holds only for a *d*-wave (DW) or *g*-wave (GW) superconductor with a zero average gap while this coefficient is significantly smaller in an anisotropic *s*-wave (ASW) superconductor.¹⁷ When the BCS gap is isotropic, the familiar “Anderson theorem,” $T_c=T_{c0}$, is satisfied^{18,19} because $a=0$ [a general expression for a is $a=\langle[\Delta(\mathbf{k})-\langle\Delta(\mathbf{k})\rangle]^2\rangle/\langle\Delta(\mathbf{k})^2\rangle$, where the angular brackets mean averaging over the Fermi surface and $\Delta(\mathbf{k})$ is the gap function]. But even in the extreme case of a highly anisotropic *s*-wave superconductor with the same nodal structure as in the DW superconductor the effect of nonmagnetic impurities on their properties remains qualitatively different although the two states are indistinguishable in phase-insensitive experiments.¹⁷ In particular we show here that the pair-breaking OIE enhancement is negligibly small based on any *s*-wave gap function that does not change sign with angle, contrary to Ref. 14.

On the other hand, the effect of *magnetic* impurities in an ASW superconductor or the effect of *nonmagnetic* impurities (or disorder) in a DW or GW superconductor can cause a significant enhancement of the isotope effects on both T_c and the penetration depth.^{20,21} Two different groups^{20,21} have consistently shown that the isotope effects on T_c and the penetration depth are almost proportional to each other provided that the strong pair-breaking effect exists. These theoretical models may be able to explain the observed large oxygen-isotope effects on both T_c and the penetration depth in underdoped cuprates if the scattering rate were large enough. However, these models cannot consistently explain the negligibly small OIE on T_c but a large OIE on the penetration depth in optimally doped cuprates.²

Differentiating Eq. (1) with respect to the ion mass, M , one can express OIE, $\alpha=-d \ln T_c/d \ln M$, in terms of the OIE observed in optimal compounds, $\alpha_0=-d \ln T_{c0}/d \ln M$

FIG. 1. (Color online) Pair-breaking enhancement of the oxygen-isotope effect, α/α_0 , in the DW superconductor (left panel) and in an ASW superconductor with the same nodal structure (right panel) as a function of the pair-breaking parameter, $1/\tau$. Symbols (left panel) represent the experimental data for Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ used in Ref. 14.

$$\alpha = \frac{\alpha_0}{1 - a\psi_1(1/2 + 1/T_c\tau)/T_c\tau}, \quad (2)$$

where $\psi_1(x) = d\psi(x)/dx$ is the trigamma function, if τ is independent of M . As shown in Fig. 1 (right panel) using Eq. (2) the maximum OIE enhancement is about 30% or less even in the extreme case of the ASW superconductor with the same nodal structure as in the DW superconductor, where the enhancement is huge, about several hundred percent or more, Fig. 1 (left panel). For a nodeless s -wave gap, hypothesized in Ref. 14, there is practically no enhancement at all. Mathematically the difference comes from the different numerical coefficients in Eq. (1): $a=1$ for DW, $a=1/4$ for the extreme ASW,¹⁷ and $a<1/4$ for a nodeless gap. Physically the difference comes from the nonvanishing, impurity-induced, off-diagonal self-energy in the ASW state, which is absent in the DW state.^{16,17}

As a result the “pair-breaking” reinterpretation of OIE by Harshman *et al.*¹⁴ with the nodeless pairing symmetry turns out to be incompatible with the experimental data. The experimental OIE, Fig. 1 (left panel), is more than one order of magnitude larger than the predicted OIE when the correct equation is applied, Fig. 1 (right panel).

One can also rule out the pair-breaking explanation of OIE (Ref. 14) even in the case of the DW order parameter, in particular in Pr substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) although there is apparently good agreement with the experiment in the case of Zn-doped YBCO, as seen in Fig. 1 (left panel). Since Zn doping induces a magnetic moment of about $0.8\mu_B$ per Zn, the data might be consistent with the magnetic pair-breaking effect in the case of an s -wave symmetry. But for YBCO with oxygen vacancies or substituted by trivalent elements for Ba, no magnetic moments and disorder are induced in the CuO_2 planes so that the impurity scattering rate may increase only slightly. In fact the low-temperature coherence length in cuprate superconductors is very small, $\xi_0 = 0.18v_F/T_c < 2$ nm, while the mean-free path, $l = v_F\tau_{tr}$, is about 10 nm or larger as follows from resistivity and recent quantum magneto-oscillation measurements in the underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (Ref. 22) (v_F is the Fermi velocity). Us-

ing these data one obtains $1/T_c\tau < 0.1$, which is too small to account for the observed enhancement of OIE with any gap symmetry as seen from Fig. 1, or for the doping dependence of the magnetic penetration depth, contrary to Ref. 14.

If however, in spite of the above estimate, Pr substitution might lead to a pair-breaking parameter, $1/T_c\tau \gtrsim 0.5$, large enough to explain the enhancement of OIE on T_c , one should expect a similar enhancement of OIE on the penetration depth because the magnitudes of the enhancement in the isotope effects on T_c and the penetration depth are nearly proportional to each other.^{20,21} Nevertheless, OIE on the penetration depth is nearly constant from the optimally doped sample to the substituted samples with a large amount of Pr,¹⁴ which is inconsistent with the theoretical prediction.^{20,21} Claiming the opposite, Harshman *et al.* have made further mistakes in their derivation of the penetration depth, λ_{ab} [Eq. (8) in Ref. 14]. They have applied the conventional correction factor $1 + \xi_0/l$ due to impurity scattering, which actually yields

$$\lambda_{ab}^2(T_c) = \lambda_{ab}^2(T_{c0})[1 + 0.36\tilde{\alpha}/T_c], \quad (3)$$

where $\tilde{\alpha} = 1/2\tau_{tr}$. Equation (3) differs from Eq. (8) in Ref. 14 with T_{c0} instead of T_c in the second term inside the square brackets. Clearly using Eq. (3) instead of the incorrect Eq. (8) in Ref. 14 one obtains an enhancement of OIE on λ_{ab} similar to that on T_c contrary to the erroneous claim of Ref. 14. Moreover the penetration-depth formula Eq. (3) is valid only for nonmagnetic impurities in s -wave superconductors that do not suppress T_c . If one assumes that nonmagnetic impurities can suppress T_c , one should consistently use a formula for the penetration depth, which is also associated with the pair-breaking effect.

We would like to emphasize here that since the pair-breaking effect in optimally doped cuprates is negligibly small and the carrier concentrations of the two oxygen-isotope samples have been consistently proved to be the same within ± 0.0002 per Cu,^{2,23} the observed large oxygen-isotope effect on the penetration depth must be caused by the large oxygen-isotope effect on the supercarrier mass. The origin of this unconventional isotope effect could arise from strong EPI that causes the breakdown of the Migdal approximation. Contrary to another misleading claim by Harshman *et al.*¹⁴ polarons accounts naturally for both OIEs, α and α_{m^*} . There is a qualitative difference between ordinary metallic and polaronic conductors. The renormalized effective mass of electrons is independent of the ion mass M in ordinary metals (where the Migdal adiabatic approximation is believed to be valid) because the EPI constant $\lambda = E_p/D$ does not depend on the isotope mass (D is the electron bandwidth in a rigid lattice). However, when electrons form polarons dressed by lattice distortions, their effective mass m^* depends on M through $m^* = m \exp(\gamma E_p/\omega)$, where m is the band mass in a rigid lattice and $\gamma < 1$ is a numerical coefficient depending on the EPI range. Here the phonon frequency, ω , depends on the ion mass, so that there is a large polaronic isotope effect on the carrier mass²⁴ with the carrier mass isotope exponent $\alpha_{m^*} = d \ln m^*/d \ln M = (1/2) \ln(m^*/m)$ as observed,² in contrast to the zero isotope effect in ordinary metals. Importantly α_{m^*} is related to the critical

temperature isotope exponent, α , of a (bi)polaronic superconductor as $\alpha = \alpha_m^* [1 - (m/m^*)/(\lambda - \mu_c)]$, where μ_c is the Coulomb pseudopotential.²⁴ The latter expression accounts for different doping dependencies of α and α_m^* as well as for a small value of α compared with α_m^* in optimally doped samples, where the electron-phonon coupling constant λ approaches from above the Coulomb pseudopotential μ_c .²⁴ Similarly, the unconventional isotope effects¹ were also explained by polaron formation stemming from the coupling to the particular quadrupolar $Q(2)$ -type phonon mode in the framework of a multiband polaron model.²⁵

In principle, a change in the oxygen mass may affect the degree and character of inhomogeneity through some unspecified mechanism, which can affect the penetration depth. However, Zhao²⁶ checked that a partial oxygen-isotope exchange causes lower oxygen-isotope effects on both T_c and the penetration depth proportional to the percentage of the isotope exchange. Another way to check if any inhomogeneity of the isotope exchange can cause the isotope effect on the penetration depth is the oxygen-isotope back-exchange experiment, where the ^{18}O sample (containing 98% of ^{18}O and 2% of ^{16}O) exchanges back to the ^{16}O sample (containing 98% ^{16}O and 2% of ^{18}O). The original ^{18}O sample and the back-exchanged ^{16}O sample have had similar oxygen-isotope inhomogeneity but both T_c and the penetration depth go back to the values of the original pure ^{16}O sample.² Hence in any case the OIE on mass must be related to EPI beyond the Migdal approximation.

Finally the claim by Harshman *et al.*¹⁴ that EPI is weak in high- T_c superconductors compared with the Coulomb coupling between carriers in buffer and CuO_2 layers contradicts the Coulomb law as follows from a simple parameter-free estimate.²⁷ EPI with c -axis-polarized optical phonons is virtually unscreened since the upper limit for the out-of-plane plasmon frequency²⁸ ($\leq 200 \text{ cm}^{-1}$) is well below the characteristic frequency of optical phonons, $\omega \approx 400/1000 \text{ cm}^{-1}$ in all cuprate superconductors. As the result of poor screening the magnitude of an effective attraction between carriers,

$V_{ph}(r) = -e^2(\epsilon_\infty^{-1} - \epsilon_0^{-1})/r$, induced by the Fröhlich EPI,¹¹ is essentially the same as the Coulomb repulsion, $V_c(r) = e^2/\epsilon_\infty r$, both on the order of 1 eV. Experimentally the strong Fröhlich EPI is validated by a huge difference in the static, $\epsilon_0 \gg 1$, and high-frequency, ϵ_∞ , dielectric constants of these ionic crystals,²⁷ $\epsilon_0 \gg \epsilon_\infty$, by recent experimental observations of a c -axis lattice expansion in pump-probe experiments²⁹ and multiple-phonon peaks in the tunnelling spectra of superconducting cuprates,^{30,31} as well as by a number of other observations including those mentioned earlier.^{2,3,5-9}

Nevertheless the basic question concerning the key pairing interaction in cuprate and other high-temperature superconductors remains open. Some local-density approximation (LDA)-density functional theory calculations^{32,33} predict small EPI insufficient to explain a kink in the quasiparticle energy dispersion observed by ARPES in cuprates. At the same time some other first-principles studies predict anomalously large EPI in cuprates³⁴ and in recently discovered iron compounds.³⁵ It is well known that LDA underestimates the role of the Coulomb correlations, predicting an anisotropy of the electron-response functions much smaller than that experimentally observed in these layered materials. So it is not surprising that EPI turns out to be rather weak in a “metallic” picture due to electron screening of the long-range electron-ion interaction. It is important that the inclusion of Hubbard U via the LDA+ U scheme significantly enhances the EPI strength³⁶ since the system becomes a doped Mott insulator with poor screening. Overall it seems plausible that the true origin of high-temperature superconductivity could be found in a proper combination of strong electron-electron correlations with a significant EPI.

To summarize we have shown that the conclusions by Harshman *et al.* (Ref. 14) are mathematically erroneous and physically at odds with the fundamental Anderson theorem and the Coulomb law.

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