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# Inverse isotope effects and models for high- $T_c$ superconductivity

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A model for high-temperature superconductivity with a mass-independent electronic mechanism in conjunction with a moderate amount of electron-phonon coupling has previously been shown to be inconsistent with experimental constraints on  $T_c$ , the isotope effect exponent, and the electron-phonon coupling. The present work allows for an electronic mechanism with an *inverse* isotope effect. In this case, the model is consistent with the experimental constraints.

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A major reason for the proliferation of models involving electronic mechanisms to explain high superconducting transition temperatures are the very small isotope effects observed in the materials with the highest transition temperatures  $T_c$ . [1-3] It is therefore necessary that models postulating electronic mechanisms explain not only the large values of  $T_c$  but also the small isotope effect. At first sight, this seems to be a trivial requirement since for most models, a purely electronic mechanism gives zero isotope effect. However, as stressed in Ref. 4, the isotope shifts are finite, albeit small, and there are experimental and theoretical estimates that indicate the electron-phonon interaction in these materials is substantial. Thus, any model based on a dominant electronic mechanism for superconductivity must also include the electron-phonon interaction, especially when calculating the isotope shift. The combined electronic and electron-phonon interactions must somehow produce a small isotope effect.

To explore the consequences of this model, the approach taken in Ref. 4 was to solve the Eliashberg equations for combined electronic and phonon-mediated pairing interactions. The electronic mechanism is represented by an attractive interaction at a particular energy,  $\omega_e$ , with a coupling strength  $\lambda_e$ , while the phonons at  $\omega_i$  couple via  $\lambda_i$ . To examine the features of this model analytically for  $\lambda < 1.5$ , we considered a McMillan equation with prefactor  $\omega_{log} = e^{(ln(\omega))}$  and a delta function model of  $\alpha^2 F(\omega)$  where

$$2\alpha^2 F(\omega) = \lambda_e \omega_e \delta(\omega - \omega_e) + \sum_i \lambda_i \omega_i \delta(\omega - \omega_i). \quad (1)$$

The two terms on the right hand side of Eq. (1) represent the electronic and phonon contributions respectively. Taking the Coulomb potential  $\mu^* = 0$  implies that

$$\alpha = \frac{\lambda_{ph}}{2\lambda} \quad (2)$$

where

$$\lambda_{ph} = \sum_i \lambda_i, \quad (3)$$

and

$$\lambda = \lambda_{ph} + \lambda_e. \quad (4)$$

As expected,  $\alpha$  is reduced by the presence of an electronic mechanism.

To determine whether it is possible to produce the observed values of  $T_c$  and  $\alpha$  for reasonable values of  $\lambda_{ph}$ , we solved the Eliashberg equations for specified  $T_c$  and  $\alpha$  (taken to be 93 K and 0.02 respectively for YBCO) by choosing an appropriate phonon spectrum consisting of Lorentzian peaks. For a given energy of the electronic mode,  $\omega_e$ , the strength of this mode relative to that of the phonon modes was varied until correct values of  $T_c$  and  $\alpha$  were obtained. It was found that the  $\lambda_{ph}$  obtained from these calculations increased as  $\omega_e$  decreased. However, even for very small values of  $\omega_e$  down to 30 meV, the resultant values for  $\lambda_{ph}$  were considerably smaller than theoretical and experimental estimates, which range upwards from  $\lambda_{ph} = 0.3$ . For still smaller values of  $\omega_e$ ,  $\lambda$  becomes unphysically large;  $\lambda \gg 10$ . It was concluded that low values of  $\omega_e$  are necessary for this model because they produce the largest values of  $\lambda_{ph}$ , but that the predicted value of  $\lambda_{ph}$  is still less than half of the smallest estimates of that quantity. As discussed in Ref. 4, it is possible that the Eliashberg model is not adequate to describe the high  $T_c$  materials because of low-dimensionality effects, a possible non-Fermi liquid ground state, or a failure to describe the electronic mechanism by the model assumed there. However, it has generally been assumed that many of the central features of superconductivity can be adequately described by the Eliashberg equations and even if this is not the case, it is still instructive to examine the consequences of the conventional theory.

Recently, it has been shown that anharmonic phonons can produce values of  $T_c$  and  $\alpha$  in agreement with experiment for the high- $T_c$  oxides,[5] and there has been

some experimental evidence for the existence of anharmonic modes. A model with large electron-phonon coupling for the anharmonic modes is capable of explaining the values of  $\alpha > \frac{1}{2}$  and the dependence of  $\alpha$  on doping in La-Sr-Cu-O.[5-7] Anharmonic phonons can also explain site selective isotope experiments.[8] Here, we take a more general point of view and consider a nonphonon mechanism (e.g. electronic) that couples to the lattice so as to produce a positive isotope shift, (i.e.  $\alpha_e < 0$ , as opposed to  $\alpha_e = 0$  for a purely electronic mechanism or  $\alpha_{ph} = 0.5$  for harmonic phonons). This mechanism is modeled as described earlier by an energy  $\omega_e$  and a coupling strength relative to the phonon modes which is determined by  $T_c$  and  $\alpha$ . Unlike previous models, we also assign a positive isotope shift to the mode by considering negative values of  $\alpha_e$ . At first sight the model appears to be restricted to the case of a mass dependent  $\omega_e$  and mass independent  $\lambda_e$ . However, for the purposes of calculating  $\alpha$ , a mass dependent  $\lambda_e$  can be formally incorporated into an effective mass dependent  $\omega_e$  which yields the same change in  $T_c$  under isotopic shift of just the electronic mode.

Experimental motivation for consideration of such an inverse isotope effect is provided by site-selective oxygen isotope effect experiments.[9] A careful choice of exchange conditions allows selective diffusion of plane oxygen sites by exploitation of the different microscopic diffusion rates. An extrapolation of site-selective isotope effect results to perfect site selection implies an *increase* in  $T_c$  of 0.32 K for  $^{18}\text{O}$  substitution in-plane with  $^{16}\text{O}$  off-plane, suggesting the presence of *some variety of a mechanism producing* an inverse isotope effect.

To illustrate the changes expected for  $\alpha_e \neq 0$ , a calculation similar to that which gave Eq. (2) yields

$$\frac{\lambda_{ph}}{\lambda} = \frac{\alpha - \alpha_e}{\frac{1}{2} - \alpha_e} \quad (5)$$

where  $\alpha_e$  measures the isotopic dependence of the electronic mode frequency. Because

$\alpha = 0.02$  is very small, even modest negative values of  $\alpha_e$  can increase  $\lambda_{ph}/\lambda$  substantially over the  $\alpha_e = 0.0$  result, as required to obtain agreement with the estimated values of  $\lambda_{ph}$ .

For more general cases, the phonon spectrum was again modeled by Lorentzian peaks and the calculations were carried out using numerical solutions of the Eliashberg equations. The electronic contribution has a strength which depends on its energy  $\omega_e$  and which is determined by the values  $T_c=93$  K and  $\alpha = 0.02$ , where  $\mu^* = 0.12$  is assumed. Results of the numerical calculations for  $\alpha_e = 0.0, -0.1, -0.3$  and  $-0.5$  are shown in Figs. 1 and 2. In all cases,  $\lambda_{ph}/\lambda$  is relatively independent of  $\omega_e$  as predicted by Eq. (3). Eq. (3) is accurate to  $\sim 25\%$ , even though it was derived for  $\mu^* = 0.0$  and  $\lambda < 1.5$ . The value of  $\lambda_{ph}$  is seen to increase rapidly with increasing  $|\alpha_e|$  for a given value of  $\omega_e$ . The shape of the curves describing  $\lambda_{ph}$  in Fig. 1 are also described well by Eq. (5) since  $\lambda_{ph} \propto \lambda$ . The total coupling strength  $\lambda$  must increase with decreasing  $\omega_e$  as shown in Fig. 2 to maintain a constant  $T_c$ ; hence  $\lambda_{ph}$  also increases for decreasing  $\omega_e$  according to Eq. (5) as shown in Fig. 1. The lower bound on the range of estimates for  $\lambda_{ph}$  in YBCO is roughly 0.3. As shown in Fig. 1, the addition of a small negative  $\alpha_e$  yields  $\lambda_{ph}$  above this value for a wide range of electronic mode frequencies. A value of  $|\alpha_e|$  as small as 0.02 yields  $\lambda_{ph} \sim 0.3$  for an electronic mode at  $\omega_e = 30$ meV.

The total coupling strength  $\lambda$  and the gap ratio  $2\Delta/kT_c$  increase with decreasing  $\omega_e$  as shown in Fig. 2, with  $\lambda$  becoming very large for  $\omega_e < 30$  meV. The gap ratio is a weakly increasing function of  $|\alpha_e|$ . Experimental values for the gap ratio up to  $2\Delta/kT_c \sim 8$  have been reported and the current calculations yield  $2\Delta/kT_c \sim 6$  for  $\omega_e \sim 30$  meV. A careful study of Raman phonon frequency shifts at  $T_c$  suggests  $2\Delta/kT_c \sim 5$ , [10] which is consistent with an electronic mode in the frequency range 40-90 meV. These relatively low frequencies are also most conducive to large values

of  $\lambda_{ph}$ , suggesting that this frequency range is most plausible for an electronic model ~~model~~ of high  $T_c$ .

The preceding analysis assumes that  $\alpha^2 F(\omega)$  is entirely due to oxygen-atom phonons. A significant portion of the coupling, particularly in the lower frequency range, could arise from non-oxygen vibrations. This situation has been modeled by using the same form for  $\alpha^2 F(\omega)$ , but assuming the the modes below 26 meV do not shift upon isotopic substitution. Since a portion of  $\lambda_{ph}$  is mass-independent, this treatment yields values of  $\lambda_{ph}$  roughly 10% larger than those previously obtained.

The site-selective isotope effect experiments provide an additional constraint on the model. These measurements are accounted for within the present model by assuming that the electronic mechanism depends exclusively on the in-plane oxygen mass. The site selective material is modeled by a spectral function in which the electronic contribution is isotopically shifted along with the planar portion of the phonon-mediated contribution. The phonon contribution to  $\alpha^2 F(\omega)$  is apportioned between planar oxygen and off-plane oxygen contributions by dividing each of the lorentzians above 25 meV into two separate peaks, one attributed to planar oxygen phonons and the other off-plane oxygen phonons. The relative strength of these two contributions is varied to obtain agreement with the site-selective isotope effect results. Since the total phonon contribution has not been modified, agreement with the full isotope effect is not affected. For  $\alpha_e = -0.3$  or  $-0.5$ , the model is consistent with the site selective results if  $\sim 75\%$  of the oxygen phonon contribution to  $\lambda_{ph}$  arises from planar oxygens. A value of  $\alpha_e = -0.1$  implies that  $\sim 50\%$  of the oxygen phonon contribution to the electron-phonon coupling arises from in-plane modes. Smaller values of  $|\alpha_e|$  require that a larger fraction of the electron-phonon coupling arise from non-planar phonons.

With a view towards the evaluation of possible physical mechanisms for a negative

$\alpha_e$ , we determine the minimal possible values of  $|\alpha_e|$  which are consistent with the site selective isotope effect and the constraint  $\lambda_{ph} > 0.3$ . For these calculations  $\mu^*$  is allowed to vary between 0.1 and 0.2 and the modes in  $\alpha^2 F$  below 25 meV are assumed to be non-oxygen. These conditions weaken the experimental constraints on  $\alpha_e$  so as to yield a more rigorous lower bound. For electronic mode frequencies below  $\sim 100$  meV, the primary constraint is the site selective isotope effect, which requires that  $\alpha_e < -0.05$ . Values of  $|\alpha_e|$  less than 0.05 imply that less than  $\sim 15\%$  of the oxygen contribution to  $\lambda_{ph}$  arises from in-plane modes, a physically implausible situation. (Without the constraint from the site-selective isotope effect, the lower bound on  $|\alpha_e|$  for a low-frequency electronic mode is reduced to roughly  $|\alpha_e| > 0.02$ .) For electronic frequencies above  $\sim 100$  meV, the primary constraint is the requirement that  $\lambda_{ph} > 0.3$ . This condition is fulfilled for  $|\alpha_e| > 0.1$ .

It is instructive to examine the way in which our calculations place restrictions on a particular model for an inverse electronic isotope shift. If it is assumed that the shift in  $T_c$  is due solely to the fractional change in lattice spacing,  $\frac{\delta a}{a}$ , under  $^{18}\text{O} \rightarrow ^{16}\text{O}$  substitution, then the shift in  $T_c$  can be estimated from the pressure dependence of  $T_c$ . [11] (The variation in  $T_c$  with pressure would also involve changes in the phonon spectrum. However, the present model implies that the electronic contribution dominates the superconductivity, suggesting that the increase in  $T_c$  under pressure can plausibly be ascribed to changes in an electronic mechanism.) The isotopic shift due to the change in lattice constant can be estimated from the isothermal compressibility and the Gruneisen constants as was done for Ge [12] and the value  $\frac{\delta a}{a} \sim 1 \times 10^{-4}$  at  $T=0$  is obtained. This yields  $\alpha_e \sim -0.005$ , roughly a factor of ten smaller than the minimal value required by our calculations. Obviously, there are other models possible for an inverse electronic isotope effect which will require a similar analysis.

In summary, we have shown that an electronic mechanism for superconductivity

in YBCO is consistent with values of  $T_c=93$  K and  $\alpha = 0.02$  as well as estimates of  $\lambda_{ph}$  if the electronic mechanism couples to the lattice in such a way as to produce an inverse isotope effect. Electronic models for high temperature superconductivity should be evaluated in terms of their ability to produce a significant inverse isotope shift.

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## FIGURES

FIG. 1. Values of the electron-phonon coupling strength,  $\lambda_{ph}$ , and the ratio of the electron-phonon coupling to the total coupling,  $\lambda_{ph}/\lambda$ , versus the energy of the electronic mode for various values of the electronic isotope shift,  $|\alpha_e|=0.0, 0.1, 0.3, \text{ and } 0.5$ . The curves are determined by the constraints  $T_c=93 \text{ K}$  and  $\alpha = 0.02$ .

FIG. 2. Values of the total coupling,  $\lambda = \lambda_{ph} + \lambda_e$ , and  $2\Delta/kT_c$  versus the energy of the electronic mode for various values of the electronic isotope shift,  $|\alpha_e|=0.0, 0.1, 0.3, \text{ and } 0.5$ . The curves are constrained by the condition  $T_c=93 \text{ K}$  and  $\alpha = 0.02$ .



