Role of anharmonicity in the high-T_c superconductors

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It is suggested that the high-transition temperatures (T_c's) observed in the superconducting oxygen-deficient perovskites may be a consequence of highly anharmonic potentials. Evidence is cited which demonstrates that the harmonic approximation fails badly for Cu^{2+} ions in a ligand field with octahedral symmetry. Since Bardeen-Cooper-Schrieffer theory and its strong-coupling extensions are based on the harmonic approximation, the reasons for their failure to describe the Cu-based perovskites can now be understood. These conclusions suggest a new interpretation for the recent results in oxygen-isotope substitution experiments. This new interpretation may be consistent with an electron-lattice mechanism for superconductivity. Surprising similarities between the heme group from hemoglobin, hemocyanin, and the oxygen-deficient perovskites are discussed. Based on these ideas, the criteria for reaching high T_c's in Ni-substituted perovskites are discussed. It is also suggested that nonperovskite materials, which have nearly degenerate, multiple-valley potential wells, may be potential high-T_c superconductors.

INTRODUCTION

I wish to point out that superconductivity in the oxygen-deficient perovskites may be due to anharmonic crystalline potentials. This idea is based on the fact that Cu^{2+} ions in octahedral symmetry have a very unusual property. Attention was first drawn by Van Vleck[1] to the peculiar features which might be expected for a $3d^9$ ion in a crystal field of octahedral symmetry with a trigonal distortion as a result of the Jahn-Teller effect. Note that the copper atoms in the La-Cu-O superconductors are in the center of an octahedra of oxygen atoms. Experiments show that the Cu ions have a valency close to $2+$.[2] The following is a very brief synopsis of material presented in greater detail by Abragam and Bleaney.[3] Two breathing modes of the copper-centered oxygen octahedra, Q_2 and Q_3, are shown in Fig. 7.26 of Ref. 3. If the calculation of the Jahn-Teller effect is carried only to order Q^2, it is found that the kinetic energy depends on $Q_2^2 + Q_3^2$, and not on the ratio of Q_2 to Q_3, as would normally be expected. The minimum energy surface is a circle in the Q_2-Q_3 phase space. This corresponds to a U(1) symmetry and the minimum energy is known as the Jahn-Teller energy. There are an infinite number of possible displacements in the Q_2-Q_3 plane which have the same potential energy. When the calculation is carried to higher order, it is found that there is a weak symmetry breaking which results in a tetragonal distortion of the octahedra. This produces a triple-valley potential well with a small barrier between the minima. When the reduction in energy due to the Jahn-Teller effect is comparable to the zero-point motion of the associated vibrational mode, the system can rapidly hop or tunnel between the three minima. This hopping is known as the dynamic Jahn-Teller effect.

Such a potential is highly anharmonic. In fact, it is probably more correct to say that it is nonharmonic. Since conventional Bardeen-Cooper-Schrieffer (BCS) theory is based on the interactions of electrons via harmonic phonons, it is not appropriate to apply this theory to a system with highly anharmonic phonons. BCS theory is

a first-order perturbation theory in which electron-electron interactions are mediated by single harmonic phonons. If the physical lattice distortions, which mediate the electron-electron interactions, are highly anharmonic, then harmonic phonons are a nonphysical and inappropriate basis set for a perturbation-theory expansion. An expansion using harmonic phonons to represent nonharmonic interactions will not converge rapidly, if at all, since higher-order terms will be important. There is no reason to expect that BCS theory should apply to a system with highly anharmonic potentials. These same considerations apply to the Macmillan-Allen-Dynes formula and Eliashberg equations, which are the strong-coupling limits of BCS theory. It is interesting to note that there are other examples of the inapplicability of BCS. Anderson claimed[4] that the former record holders for the highest T_c, the $A15$'s, could not be described by BCS theory. He suggested that the reason for the breakdown of BCS theory in the case of the $A15$'s was that the molecular potentials were anharmonic. Several of the anamolous features of the $A15$'s also appear in the oxygen-deficient perovskite superconductors. In support of this idea, Yu and Anderson[5] show that superconductivity can result from noninteracting anharmonic oscillators. Krumhansl and Schrieffer[6] have also addressed the problems of phase transitions and the breakdown of perturbation theory for anharmonic potentials.

There are several reasons which make the nonharmonic hypothesis attractive. First, *there is no a priori reason to expect that the harmonic approximation should hold for all materials.* Many mechanisms have been suggested to explain superconductivity in the oxygen-deficient perovskites; there is to date only one demonstrated mechanism for superconductivity, namely electron-phonon interactions. One's first inclination in attempting to solve the high-T_c puzzle should be to look for solutions which exhibit the least radical departure from the successful theory. Thus, electron-lattice interactions should generally be given more weight than more exotic mechanisms, such as excitons, plasmons, etc., which have never demon-

strated superconductivity. Another attractive feature of this hypothesis is that only Cu^{2+} and Ni^+ have this peculiar potential. This fits in nicely with comments made by both Anderson and Scalapino[7] who think copper plays a special role in the phenomenon. In fact, there have been other copper compounds, such as copper chloride, which had given early, but irreproducible indications of high-temperature superconductivity.

NONHARMONIC POTENTIALS AND THE ISOTOPE EFFECT

One question that must be answered is, can the high values of T_c be explained by nonharmonic potentials in a way that is consistent with the recent results on the isotope effect? Recently, Batlogg et al.[8] performed experiments in which ^{16}O was replaced by ^{18}O. The Eliashberg equations in the weak-coupling regime predict that the critical temperature depends on the vibrational frequency of the relevant phonon modes. It is generally believed that coupling to the breathing modes of the oxygen octahedra is the most likely electron-phonon coupling mechanism. It is expected that an isotope substitution should result in a shift in the vibrational frequency, thus changing the critical temperature T_c. Infrared (ir) spectra were taken for the ^{18}O substituted samples and the breathing mode vibrational frequency of the oxygens was observed to shift as expected. This result has been taken as evidence that the superconductivity mechanism is not due to electron-lattice interactions, since there was no corresponding shift in T_c. However, in the strong-coupling limit, the solutions to the Eliashberg equations become independent of the atomic mass. This occurs because the very strong electron-phonon interaction causes a softening of the phonon. *Softening of the phonon mode can be associated with an insensitivity of T_c to isotope substitutions and to the corresponding frequency shift.* The appearance of an ir absorption peak at the frequencies expected for the breathing modes of the oxygen octahedra, and the unambiguous isotope effect on these vibrational frequencies, has been taken as evident that there is no significant softening of the oxygen breathing mode. However, in high anisotropic materials such as oxygen-deficient perovskites, it is not at all clear that the coupling of the breathing modes to the conduction electrons should be the same for a different mode. It is conceivable that one mode couples very strongly to the conduction electrons (large λ–strong-coupling limit) while the other modes (small λ–weak-coupling limit) do not. Given the data, it is possible that there is a strongly coupled, low-frequency (softened) oxygen breathing mode that is responsible for the superconductivity. It is very suggestive that this sort of mode softening is exactly what happen for a Cu^{2+} ion in an octahedral symmetry, as described in Ref. 3. Is it possible that the nonharmonic mode is a breathing mode which has been softened by strong coupling?

If the copper atom sits in an anharmonic potential and is the source of the superconductivity, then the resolution of the isotope puzzle is even easier. For an anharmonic potential, the limits on T_c, which have been calculated using the Eliashberg equation, are not applicable.

The heme group of hemoglobin appears to have many features in common with the oxygen-deficient perovskites.[9] The heme group consists of a $3d$ ion iron in the center of the ligand field of four, square-planar nitrogens. Thus, the iron and nitrogens are linked by $3d$-$2p$ orbitals, as are copper and oxygen in the perovskites. In the hemoglobin protein, the heme group occur in coaxial pairs separated by about 6 Å. When bonded to an O_2 molecule which fits between the Fe ions in the heme rings, the Fe ion sits in an octahedra ligand field. In this state, known as oxyhemoglobin, the Fe ion has a valency of $\approx 3+$ and a spin $S = 0$. Without the O_2 molecule, the iron ions are fivefold coordinated, have a valency of $\approx 2+$, and a spin of $S = 2$. This is known as deoxyhemoglobin. In oxyhemoglobin, the Fe ion sits roughly in the plane of the heme ring. In deoxyhemoglobin, the Fe ion moves approximately 0.3 to 0.4 Å out of the plane of the heme ring.[10] *Thus, the valency change of the Fe is associated with an enormous structural distortion.* By comparison, typical displacements due to phonons are less than 0.1 Å. The Fe ion in oxyhemoglobin sits in an octahedral ligand field and undergoes a Jahn-Teller distortion which is *very* similar to the Jahn-Teller effect in the perovskites. The cubic symmetry distorts to a tetragonal symmetry with a small admixture of rhombic distortion. The two valency states found in oxyhemoglobin and deoxyhemoglobin have essentially the same degree of tetragonal distortion, but differ in the degree of rhombic distortion. The sixfold coordination of the Fe ion in oxyhemoglobin is the same as is found in the CuO_6 octahedra of $La_{1.85}Sr_{15}CuO_7$. The fivefold coordination of the Fe ion in deoxyhemoglobin is the same as is found in the CuO_5 pyramids of $YB_2Cu_3O_7$. The separation between the Cu-O planes in the oxygen-deficient perovskites is very similar to the separation between the heme rings in hemoglobin (~ 6 Å). The Jahn-Teller transition also causes a slight tilting ($\approx 4°$) of the plane of the heme ring. It has been suggested that the unusually large coupling between valency and structural distortion in hemoglobin is a result of the dynamic Jahn-Teller effect. *The energy levels of the two different valency states are almost degenerate,*[9] *enabling the Fe ion to change valence readily.* This suggests that the system has a very anharmonic potential and very strong "electron-phonon" coupling. In fact, the ability of the heme group to make a large structural change with a small cost in energy gives rise to cooperativity, a feature essential to the function of the hemoglobin protein. Perhaps the heme group was selected by evolution because of its anomalously large coupling between charge state and structure.

The similarities between hemocyanin and the copper-based, high-T_c superconductors are even stronger. Hemocyanin is the oxygen-carrying protein in the blood of molluscans and arthropods. In hemocyanin, a Cu^{2+} ion plays the same functional role as the Fe^{2+} ion in hemoglobin. Although, less is known about hemocyanin, it is thought[11] that the active oxygen binding site consists of a Cu^{2+} ion which sits in a tetragonally distorted, ligand field. As in hemoglobin, bonds to an O_2 molecule form a bridge between a pair of Cu^{2+} ions. The Cu pairs are antiferromagnetically coupled and the binding to oxygen is associated with a change in the valency of the Cu ions. Since

cooperativity is also an important feature of the functioning of hemocyanin, it follows that the binding of the O_2 molecule and the change in the valency of the Cu ions is linked to a large structural distortion of the ligand field and of the atoms surrounding the Cu ion.

Based on the analogy with hemoglobin, we can now make a conjecture on the nature of the superconducting mechanisms. From the behavior of the heme pair in hemoglobin and hemocyanin, we can be reasonably confident that the Cu^{2+} ion sits in a nearly degenerate, double-valley potential well. The analogy with hemocyanin is even stronger. Symmetry suggests that there is one double valley well on each side of the Cu-O plane. Like hemoglobin, a change in the ligand field, which is perpendicular to the Cu-O plane, should induce a Jahn-Teller transition. Due to the extreme instability associated with the dynamic Jahn-Teller effect, charges moving through the oxygen-deficient perovskites can induce a very large change in the position of the Cu atom. As in hemoglobin, the Cu atom will move from a position near the Cu-O plane to a position which is substantially above (or below) the plane. This structural shift will be associated with significant charge transfer. Thus, the moving charge will leave behind it a wake of CuO_6 octahedra (CuO_5 pyramids) with large structural distortions and an unusually large polarization cloud. The large charge transfer will produce strong "electron-lattice" interactions. The high values of T_c result from the strong coupling of the charges to the dynamic Jahn-Teller effect (DJTE) excitations.

The role of the one-dimensional Cu-O chains in the $Y_1B_2Cu_3O_7$ materials can be conceptualized in terms of Little's[12] model for a high-temperature superconductor. The Cu-O chains play the role of the one-dimensional conductor in Little's model. The CuO_5 pyramids are adjacent to the Cu-O chains and play the role of the polarizable sidechains. DJTE excitations of the CuO_5 pyramids play the role of the excitonic excitations in Little's model.

CONCLUSIONS

If this reasoning is correct, then it suggests that high T_c's might result if Cu^{2+} in an octahedral symmetry is replaced with the other $3d^9$ ions, Ni^+ or Co^0. However,

some care must be exercised when doing this. Since it is thought that the conductivity in the perovskites is the result of the fortuitous overlap of the energy level of the copper $3d$ orbitals with the oxygen $2p$ orbitals. For example, it is quite possible that the conductivity will disappear if all the coppers were replaced with nickel atoms. This would occur if the energy levels of the nickel $3d$ orbitals were different than the energy of the oxygen $2p$ orbitals. Thus, it would probably also be necessary to replace the oxygens with an atom that has orbital energies compatible with the nickel. Since the energy levels of the Ni and the Cu ions are different, it is expected that the introduction of a small number of Ni ions would localize states in the Cu-O conducting band. Thus, it is probably necessary to replace all of the copper atoms with nickel.

Materials which are expected to have highly anharmonic potentials should make good candidates for high-T_c superconductors. Systems exhibiting the dynamic Jahn-Teller effect or those possessing multiply degenerate potential wells with atoms which can hop between the minima should be examined for signs of superconductivity. For example, the anharmonic potential of the heme group might also be a feature of other metalloporphyrins or other metallomacrocycles with a square planar geometry in the center.[13] One possible road to DJTE superconductivity is to synthesize 1D conductors with sidechains which can exhibit the dynamic Jahn-Teller effect. As an example of such a system, one could attach metalloporphyrin sidechains to a conducting polymer such as polyacetylene (PA). The metalloporphyrin should be attached to the chain via an O atom or an N atom. The porphyrin should also have ligand fields on both sides of the porphyrin plane and perpendicular to the plane. The bond between the metal atom (M) from the metalloporphyrin and the C atom on the PA backbone would be M-O-C. For the first attempts, it is probably a good idea to use Cu, Ni, or Fe as the M in the porphyrin. For later attempts, other $3d$ transition metal ions should be tried. Even if the above conjectures on the role of the DJTE in the new high-T_c materials turn out to be incorrect, it is probably a good idea to explore further the possibility of DJTE superconductivity further. If such systems can be realized, they should have high T_c's.

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