Anomalous Properties and Micromorphology of $YBa_2Cu_3O_7$

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(Received 12 January 1990)

Anomalies in vibrational spectra measured by neutron and Raman scattering and spatial inhomogeneities in ^{18}O-^{16}O exchange lead to a two-region micromorphological model of YBCO. This model explains why among "single-phase" high-temperature superconductors only YBCO exhibits a nearly zero isotope effect. This small isotope effect has been used as the justification for many exotic nonphonon models of high-temperature superconductivity, but the present discussion shows that such models are unnecessary.

PACS numbers: 74.20.Fg, 78.30.Er

Of all the high-temperature superconductors (HTSC), $YBa_2Cu_3O_7$ (YBCO) is the best characterized and most extensively studied. It exhibits a number of anomalies that are absent from simpler single-phase HTSC, such as $Ba(Pb,Bi)O_3$, $(K,Ba)BiO_3$, and $(La,Sr)_2CuO_4$. The most dramatic of these is the (nearly) zero isotope effect,[1] which has led to much speculation concerning exotic nonphonon microscopic superconductive mechanisms.[2] Because of this effect some have even asserted[3] that conventional electron-phonon coupling as a source of HTSC is "unthinkable."

In this Letter I analyze three structural anomalies in YBCO and its alloys, and I show that all three anomalies, although indirect, can be explained by assuming that YBCO has a complex micromorphology which is not revealed by ordinary diffraction experiments. This morphology probably consists of microdomains of diameter d and domain walls of width w, and it could represent the earliest stage of spinodal decomposition which would occur if the samples were in equilibrium.[4] The superconductive properties of the domain walls and domain interiors are drastically different as are the structures, and this can easily explain the nearly zero isotope effect. Such a morphological instability is a specific example of one of the lattice instabilities[2] which always limited T_c in superconductors like NbN or Nb_3Sn, but here it has a much more complex form because of the propensity of oxides to form ferroelastic domains, and because of the extraordinary complexity of the thirteen-atom layered unit cell of YBCO.

Traditionally domain structure is difficult to observe, and it can easily be overlooked in diffraction experiments which heavily weight coherent scattering from domain interiors while the domain walls contribute only to the background, which is always large in HTSC (large R values $\gtrsim 0.1$ in structure refinements). The first indirect evidence for a domain micromorphology which I discuss is the generalized vibrational density of states $G(\omega)$ measured by incoherent neutron scattering[5] for $A = YBa_2Cu_3O_{6.9}$ and $B_1 = YBa_2Cu_3O_{6.1}$ and $B_2 = Y_{0.5}Pr_{0.5}Ba_2Cu_3O_7$. The data are reproduced in Fig. 1 for the reader's convenience. The most remarkable, but perhaps the least obvious, feature of the data is that the change from A to B_2 (alloying in the Y plane) is quantitatively smaller but qualitatively similar to the change from A to B_1 [reduction of the Cu(1)-O(1) chains], especially the decrease in $G(\omega)$ between 40 and 60 meV, and the formation of a new peak near 81 meV. A normal-mode analysis[5] based on a shell model was unable to identify the origin of the 81-meV peak, but it did show that the 40-50-meV region is due almost entirely to the Cu(2)-O(2)-O(3) planes. The anomaly is now clear. Interatomic forces are short range, and we do not expect chemical changes in the Y or Cu(1)-O(1) planes to have such drastic effects on the vibrations of the Cu(2)-O(2)-O(3) plane. If we try to explain these changes through interplanar couplings, we are stymied because they imply force-constant changes $\Delta k/k \sim \Delta\omega^2/\omega^2 = 0.2$ or $\Delta\omega^2 \sim 500$ meV^2, which would make

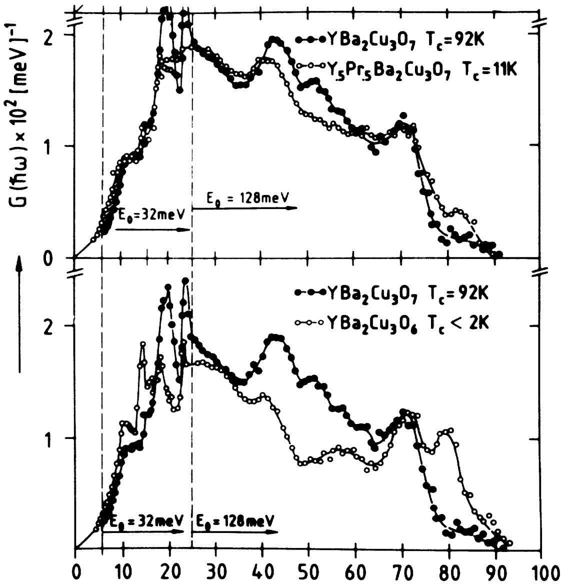

FIG. 1. Comparison of the effective phonon density of states $G(\omega)$ measured by neutron scattering on $A = $ YBCO and $B = Y_{0.5}Pr_{0.5}Ba_2Cu_3O_7$ and $YBa_2Cu_3O_6$. Data from Ref. 5.

some of the Y or Cu(1) modes below 20 meV unstable ($\omega^2 < 0$). Finally, no force-constant model can explain why B_1 (Y-plane substitution) and B_2 [Cu(1)-O(1) reduction] should have qualitatively similar effects. However, micromorphologically we expect spinodal decomposition in A ($T_c \sim 90$ K) but not in B_1 or B_2 ($T_c \sim 0$). Thus the similarity between B_1 and B_2 merely reflects their lack of domain walls, the 81-meV B peak represents a point defect band in an otherwise periodic crystal, and the additional structure in $G(\omega)$ for A = YBCO near 55 meV is due to the domain walls, as is the long tail above 80 meV. The tail in A could be the B defect peak broadened by strong interactions if the B defects have clustered in forming A domain walls. The strength of the extra A peak at 55 meV corresponds to a filling factor of approximately $w/d \sim 0.1$.

The second anomaly has been discovered in a very complete study[6] of the temperature and composition dependence of the 340-cm^{-1} Raman-active band associated with O(2)-O(3) vibrations normal to the Cu(2)-O(2)-O(3) plane. This band has attracted great interest because its frequency softens by 3% below T_c. The anomaly is that its bandwidth should narrow if part of the lifetime broadening is intrinsic once the vibrational frequency falls below the energy gap $E_g \sim 500$ cm^{-1}. This narrowing is expected theoretically and it has been observed experimentally[7] in Nb_3Sn. However, here phonon softening is associated with an *increase* in bandwidth, as shown in Fig. 2, again for the reader's convenience. Note that both the softening and the anomalous broadening are large in $YBa_2Cu_3O_{7-x}$ only near $x=0$ ($T_c = 90$ K) and both have virtually disappeared when $x = 0.32$ ($T_c = 60$ K). One might think[8] that the broadening is associated with states in the gap which are present in $YBa_2Cu_3O_7$ but not in Nb_3Sn, but this explanation is inadequate for two reasons. First, theory would say that some states are removed from the gap by the superconductive phase transition, so the most that the remaining states could do would be to reduce the rate of band narrowing; they could not lead to intrinsic band broadening. Second, there is growing evidence[9] that the states in the gap are an intrinsic feature of HTSC, and they should be present even when $x = 0.32$, when the anomaly has disappeared.

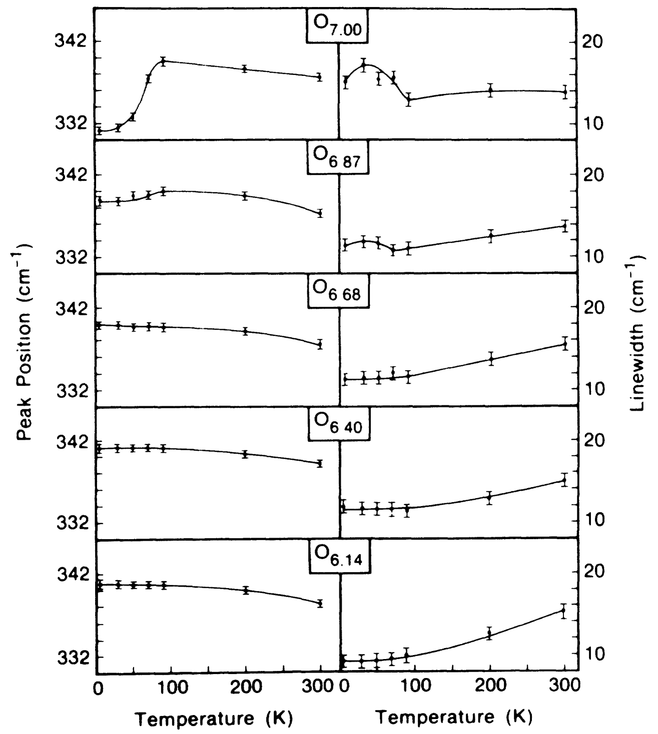

FIG. 2. Temperature-dependent peak positions and linewidths (full width at half maximum) of the 340-cm^{-1} mode in $YBa_2Cu_3O_x$, from Ref. 6.

We can now see that the micromorphological domain model can easily explain the anomalous broadening as the result of a decrease in the superconducting order parameter $|\Psi^2|$ near the domain walls, which function as weak links. This produces inhomogeneous broadening of the strongly electron-phonon coupled[10] 340-cm^{-1} mode. Exotic nonphonon mechanisms[2] for HTSC can explain neither the phonon softening nor the band broadening, because they are predicated on purely electronic interactions in a homogeneous material.

The third anomaly has been discovered in the context of very careful studies of the isotope effect itself. This oxygen diffusivity of $YBa_2Cu_3O_{7-x}$ is very high, and this makes it easy to replace ^{16}O by ^{18}O by annealing in an ^{18}O-enriched (96%) flowing gas at high T ($\lesssim 700\,°C$, but still much lower than the original oxidation temperature $T_f \sim 950\,°C$) for long times. There are three surprises here. Studies of Raman and infrared optically active vibrational modes have shown[11] that the measured isotope shifts correspond to nearly complete ^{18}O exchange at all sites in the crystalline unit cell, that is, achievement of isotopic equilibrium between sample and flowing gas. Yet mass spectrographic measurements of ^{16}O and ^{18}O content show that no more than 90% exchange has ever been achieved by any of the fifteen groups which have reported their results.[12] Where is the ^{16}O that has not been exchanged, and why does it not show up at any of the crystalline sites observed in the optical spectra? Second, the isotope exchange might have been diffusion limited, so that the missing ^{16}O is located in the cores of the sample grains not probed optically. However, two separate secondary-ion mass spectroscopy experiments[12,13] have shown that isotopic equilibrium is achieved in the granular cores, while the concentration of the unexchanged ^{16}O is largest in the granular surface layers, and it increases to $\lesssim 20\%$ in the optically probed region. What is the cause of this inverse isotopic inhomogeneity? Third, with so much ^{16}O near the surface, why do the observed isotope shifts agree so well with those predicted by theory assuming 100% exchange?

All of these results appear anomalous if the samples are supposed to be homogeneous, but they are readily explained by the micromorphological domain model. Because of surface stress the domain-wall filling factor w/d can increase near the surface. The ^{18}O can exchange in the domain interiors but not the domain walls. The observed Raman and infrared bands would originate from the domain interiors, where exchange is nearly complete.

The large filling factors $w/d \simeq 0.1$ suggested here naturally arouse our curiosity as to the value of d itself. The domains discussed here are not twins,[14] which occur on a scale $\gtrsim 2000$ Å, and which have a filling factor $w/d \lesssim 10^{-3}$. They might be associated with orthorhombic fluctuations[15] which have been observed on a scale of 1000 Å, but these fluctuations would still not have the drastic effect on $G(\omega)$ required for Fig. 1. Instead I believe that the best measure for d is provided by ion-implantation damage,[16] which clusters on a scale of 100 Å. The observed damage acts as a marker indicating an upper limit for the average spacing of the native domain walls. These domains are orientationally coherent, which is why they are so difficult to observe by diffraction. Orientationally coherent microdomains are probably more common than is generally realized. They were observed some time ago in "amorphous" Si films,[17] and they have recently been identified in "stable" quasicrystals.[18] Here the domain walls probably arise as the result of orthorhombic internal stress associated with filling the O(1) sites of the Cu(1)-O(1) plane, which causes buckling of this plane and excess O(1) vacancies in the domain walls compared to the domain interiors.

We now come to the celebrated (nearly) zero isotope effect in YBCO, with $T_c \propto M^{-\alpha}$, where M is the isotopic mass and $\alpha = 0.5$ in an ideal homogeneous crystal with a featureless electronic structure near E_F and electron-phonon coupling only to oxygen modes. Typical values for α in Ba(Pb,Bi)O$_3$, (K,Ba)BiO$_3$, and (La,Sr)$_2$CuO$_4$ range[19-21] from 0.15 to 0.35, which may represent the degree of dominance of oxygen modes, while[1,12] $\alpha \lesssim 0.03$ in YBCO, which is therefore anomalous.[22] But we see that this anomaly is easily explained without recourse to exotic nonphonon models.[2,3] Just as the ^{18}O distribution itself is affected by ferroelastic stresses, the ^{18}O concentration must couple to these stresses, which ultimately determine the w/d ratio, which in general will change when ^{16}O is partially replaced by ^{18}O. But T_c itself represents a compromise between an effective $T_c \gtrsim 100$ K for the domain interiors and $T_c \lesssim 60$ K in the "weak-link" domain walls, and the weight given to the two regions depends on w/d, itself a function of isotopic concentration. Thus the measured isotope effect can have a wide range. One could even have $\alpha < 0$ if w/d were much smaller for ^{18}O-enriched samples than for ^{16}O-enriched samples. Such a sign reversal is well known[23] for PdH$_x$ and PdD$_y$.

From a materials point of view the present close analysis of the data has far-reaching theoretical implications. We have vindicated (not for the first time) Ockham's razor, which asserts that one should not make additional assumptions (such as exotic nonphonon mechanisms) merely to generate novelty for its own sake. We have uncovered micromorphological native defect clustering to form domain walls, but this suggests a high density of unclustered native defects which can act as interlayer electrical bridges, which play a pivotal role in quantum percolation theory (QPT).[9,24-26] The contrast between the present analysis and the exotic theories[2,3] shows how important to the theory of HTSC detailed knowledge of experiment is.[27] However, the general phenomenological principles discussed here do have predictive value. After the nearly zero isotope effect ($\alpha \simeq 0$ in YBCO) was discovered,[1] I predicted,[28] contrary to Ref. 3, that α would not be nearly zero in oxide superconductors with lower T_c's. Specifically I suggested $\alpha \sim 0.2$ in La$_{2-x}$Sr$_x$CuO$_4$ ($T_c = 38$ K) with $x = 0.15$. My prediction proved to be in good agreement with experiment [$\alpha = 0.15(1)$].[21] For strong electron-phonon coupling I also noted the likelihood that internal coordinates associated with oxygen vacancies could be used to "screen" or compensate isotopic shifts in electron-phonon interactions, much as internal relaxations reduce the thermal expansion of oxide glasses. Finally, the present theoretical model is the only one which identifies and consistently explains these previously unrelated vibrational and isotopic anomalies in a unified way.

Note added.—After this paper was completed, dramatic channeling anomalies were reported[29] for YBCO. These data are consistent with substantial internal rearrangements occurring near $T_c(\alpha)$ and $T_c(\beta)$ in a two-region sample with one region α having a local $T_c(\alpha) \gtrsim 120$ K. The effect of these rearrangements on the ion-channeling minima $\chi_{\min}$(Cu) and $\chi_{\min}$(O) are themselves anomalous and cannot be described merely by phonon softening; hence reconstruction of the type described in the present model is strongly suggested. Note that the O anomaly, measured with *decreasing* temperature, shows *decreasing* disorder below 120 K. This suggests that at least in one region local superconductive fluctuations (possibly associated with quasi-one-dimensional CuO chains) are coupled to increasing O planarity. (Such one-dimensional fluctuations are not diamagnetic.) Note also that at least the initial decrease, centered on 120 K, cannot be an artifact associated with damage. The anomalously rapid increase in planarity is expected to couple to improved (super)conductivity according to QPT.[30] Electron-energy-loss spectroscopic data[31] also show local superconductivity at $T = 116$ K in YBCO. The interpretation of these data is complicated by surface structure and beam damage, but the loss edge which persists to above T_c is still related to (local) superconductivity.[31] The temperature dependence of the height H of the electron energy loss which occurs at the superconductive energy gap [Fig. 3(b) of Ref. 31] exhibits an only slightly rounded linear drop beginning near $T_p/T_c = 0.75$. This drop can be explained in terms of percolation of the phase of the superconductive order parameter (Cooper-pair amplitude) Δ, which is quenched by thermal fluctuations when $\xi = \xi_0(1 - T_p/T_c)^{-1/2}$ is equal to the domain radius $r = d/2$. With $\xi_0 = 30$ Å this gives $d = 120$ Å, in agreement with the estimate above.[16]

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