Is the Isotope Effect Absent in $YBa_2Cu_3O_{7-\delta}$?

The mechanism responsible for the high-temperature superconductivity in the recently discovered metallic oxides is the key theoretical issue in this field at the present time. For this reason the presence or absence of an isotope effect is extremely important since it provides a clue as to whether the conventional mechanism for superconductivity can be discarded. In two recent articles[1,2] it was reported that the substitution of the isotope ^{18}O in $YBa_2Cu_3O_{7-\delta}$ prepared with ^{16}O has no perceptible effect on the superconducting transition. In the present Comment we show that these two experiments do not provide an *unambiguous* proof for the absence of the isotope effect and therefore that a mechanism involving phonons could still be important for high-temperature superconductivity.

The samples used in the above-mentioned experiments were synthesized with ^{16}O solids which were later replaced with ^{18}O. In one case[1] at most 74% $\pm$ 7% of the ^{16}O was replaced by ^{18}O. In the other case,[2] 90% of the evolved oxygen was ^{18}O but only 50% of the oxygen was evolved so that in principle only 45% of the ^{16}O can be guaranteed to have been substituted. Since there are four inequivalent oxygen sites in this structure, in order to conclude from these measurements that there is no isotope effect, it is necessary to assume that the oxygen substitution does not occur preferentially.

Detailed neutron-diffraction studies,[3] however, show that the different sites evolve oxygen with various degrees of difficulty. For instance, the O1 sites evolve oxygen at very low temperatures; on the other hand, very little evolution of oxygen was observed from the O2, O3, and O4 sites in samples heated up to 900 °C. Furthermore, the Cu1–O4 bond distance ($\simeq$1.850 Å) is very short compared to the other metal-O distances,[4] suggesting that it may be difficult to exchange the O4 oxygen.

In principle, since Raman scattering provides information on the vibration of the O2, O3, and O4, it should be possible to determine if these sites have been populated with ^{18}O. Unfortunately, out of the four Raman lines presented in Ref. 1 as evidence of substitution, it has been shown that[5,6] only the line at 501 cm^{-1} can be unambiguously assigned to $YBa_2Cu_3O_{7-\delta}$. Our current Raman work[5] on other rare-earth compounds of the $YBa_2Cu_3O_{7-\delta}$ type leads us to believe that the 500-cm^{-1} line is due to vibrations of O2 and O3, leaving open the possibility that oxygen on the O4 sites (29% of the total amount of oxygen) has not been replaced in the reported experiments. This fact, together with claims that the electronic structure is very sensitive to the O4 positions,[7] and that the O4-containing chains are crucial for the existence of superconductivity,[8] is sufficient to leave some doubt as to whether the isotope effect is really absent. Further experiments, including the examination of samples prepared from pure metals and *only* ^{18}O, should be performed in order to clarify the issues raised here.

Since the submittal of this article, a small isotope effect has been reported.[9] The questions we have raised here, however, remain valid; viz., if there is preferential oxygen substitution the conclusions regarding the magnitude of the effect should be revised.

This work is supported by the U.S. Department of Energy, Basic Energy Sciences, Materials and Chemistry Sciences, under Contract No. W-31-109-ENG-38.

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Received 7 August 1987
PACS numbers: 74.70.Vy, 74.30.Ek

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