Effect of isotopic substitution of copper on the critical temperature of the superconducting ceramic $Y_1Ba_2Cu_3O_7$

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Electrical measurements reveal no effect of a substitution of the isotopes ^{63}Cu and ^{65}Cu on the critical temperature of the high-temperature superconductor $Y_1Ba_2Cu_3O_7$. The absence of an isotopic effect involving copper, along with the absence of such an effect involving the other elements, is interpreted as evidence in favor of a nonphonon mechanism for the high-temperature superconductivity.

After the discovery of high-temperature superconductivity, the mechanism for the onset of this superconductivity became an exceedingly important question. "Ordinary" (low-temperature) superconductivity is provided by electron pairs which are produced through the exchange of phonons. It has not been established experimentally[1] that high-temperature superconductivity also arises because of the formation of electron pairs. The specific mechanism by which these pairs are created has not been established. In ordinary superconductors, the critical temperature T_c nearly always depends on the phonon frequency and thus on the mass of the lattice ions. According to the standard BCS theory, we would have

$$T_c \propto M^{-\alpha}, \qquad (1)$$

where M is the mass of the lattice ions, and $\alpha = 1/2$. Experimentally, the isotopic effect, which has been studied for a wide range of superconducting materials, usually leads to values of α between 0.2 and 0.5.

For the high-temperature superconductor $Y_1Ba_2Cu_3O_7$, it would seem to be interesting to study the isotopic effect for all of the elements other than yttrium: The replacement of yttrium by most of the rare-earth elements has only a slight effect on

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the critical temperature.[2] We would naturally expect to see the greatest isotopic effect in the case of oxygen. However, Bourne *et al.*[3] report that the replacement of ^{16}O by ^{18}O has no significant effect: $\alpha = 0.0 \mp 0.027$. Leary *et al.*[4] found that the replacement of ^{16}O by ^{18}O, which was nearly perfectly reversible, resulted in a decrease of 0.3–0.5 K in the critical temperature. This decrease is about an order of magnitude smaller than that which would be estimated from relation (1) with $\alpha = 0.5$. Batlogg *et al.*[5] carried out a parallel study of the Raman spectra of samples of this ceramic and found that a 75% isotopic substitution of oxygen leads to a 4% change in the phonon frequency but only a 0.2% shift of T_c. More recently, Felner *et al.*[6] described a replacement of oxygen by sulfur and the production of polyphase $Y_1Ba_2Cu_3O_6S_1$ samples. Again, this replacement caused no significant shift of T_c; this negative result can apparently be interpreted as an argument in favor of the assertion that T_c does not depend on the mass of the oxygen.

Can oscillations of other ions influence the critical temperature?

Our measurements with the isotopes ^{63}Cu and ^{65}Cu show that there is no shift of T_c.

The samples for the present experiments were prepared in the following way. The first step is to press tablets $25 \times 7 \times 1$ mm in size at a pressure of 10 kbar from thoroughly ground powders of Y_2O_3, BaO_2, and the isotopic cupric oxide. These tablets are then sintered at 950 °C for 3 h in air. The samples are then cooled slowly at a rate on the order of 1 deg/min. In preparing one sample we used cupric oxide with a 99.7% concentration of the isotope ^{63}Cu, and for the second sample we used cupric oxide with a 99.0% concentration of the isotope ^{65}Cu. We took particular care to insure that all conditions would be identical in the preparation of the two samples.

We measured the temperature dependence of the resistance by a four-contact method. These measurements were carried out in parallel for the two samples, which were held in a constant-temperature chamber, in which the temperature was varied slowly enough that there was no discernible difference between the results measured during heating and cooling. In the normal state, the two samples had resistivities which were equal within about 1% (the values were a few milliohm·centimeter). Their resistivity varied with the temperature in a metallic fashion. The decrease in the resistance near T_c occurred fairly sharply: from the 90% level to the 10% level in an interval of about 1 K. For these samples we found

$$\Delta T_c = T_c(^{63}Cu) - T_c(^{65}Cu) = 0{,}2\ K. \quad (2)$$

After the measurements the samples were again ground into powders, pressed into tablets, and annealed as before. Measurements taken from these newly produced tablets showed that the transition was stretched out over an interval about twice as long and that there was a change in the sign of the temperature shift:

$$\Delta T_c = T_c(^{63}Cu) - T_c(^{65}Cu) = -\ 0{,}1\ K. \quad (3)$$

Yet another cycle of grinding, pressing, and annealing of the samples stretched the transition out over about 3 K. In this case we found, within an error on the order of 10^{-2} K,

$$\Delta T_c = 0. \quad (4)$$

On the average over the three measurements, we thus have

$$\alpha = 0.01 \mp 0.03 \quad (5)$$

Control measurements with pairs of samples with natural copper also revealed a scatter in the values of ΔT_c over the interval 0.1–0.2 K.

Bourne *et al.*[7] have recently published another result of their research on the copper isotopic effect and also the barium isotopic effect. They showed that the replacement of copper isotopes leads to $\Delta T_c = T_c(^{63}\mathrm{Cu}) - T_c(^{65}\mathrm{Cu}) = -0.2$ K, while the replacement of barium isotopes leads to $\Delta T_c = T_c(^{135}\mathrm{Ba}) - T_c(^{138}\mathrm{Ba}) = -0.1$ K.

In summary, all the experimental data presently available indicate that there is absolutely no isotopic effect in the ceramic $Y_1Ba_2Cu_3O_7$ or that, at the very least, this isotopic effect is much smaller than that predicted by the standard phonon mechanism. The small shifts in the critical temperature which are observable are of a random nature, stemming from nonreproducible differences in the preparation of the samples. This result implies that the high-temperature superconductivity may arise by virtue of a nonphonon mechanism for the pairing of electrons.

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