

Batlogg, Cava, and Stavola Reply: An experimental study cannot decide whether the isotope effect is present or absent in the 1-2-3 superconductors,¹ but it can give numerical limits for its magnitude. In this spirit we concluded² that our experimental results "indicate very little, if any, of an isotope effect," and give an upper limit of 0.02 for the isotope effect exponent α , obtained under the carefully controlled conditions described in Ref. 2. A somewhat larger upper limit was estimated by Bourne *et al.*³ Recently, a small nonzero isotope effect ($0.035 < \alpha < 0.05$) was reported⁴ when experimental procedures similar to ours² were adopted, but the oxygen isotopes were exchanged at 900–950°C instead of at 500°C.² This result again confirms that the oxygen isotope effect is indeed very small.

The main motivation for the Comment by Grimsditch *et al.*¹ is to point out the possibility of a preferential site for oxygen isotope substitution. It is suggested that oxygen in the "bridging" position between the Cu-O chains and the Cu-O planes might not have been exchanged. While the creation of a vacancy on this site may or may not be favorable, that does not imply, however, that this site should not be involved in oxygen diffusion within the crystals. To the contrary; since a large fraction of the O sites in the Cu-O planes are occupied by ¹⁸O, and the isotopes enter the crystals by exchanging through the Cu-O chains, it is likely that the bridging sites are also occupied by ¹⁸O.

The most useful starting point for discussions of the isotope effect is the comparison of phonon frequency shifts and variations in T_c . Therefore, we measured the Raman spectra in the ¹⁶O- and ¹⁸O-rich samples.^{2,5} Although minor ambiguities exist regarding mode assignments, we reject the interpretation offered in the Comment, particularly the claim that only one line in our original reported spectra is intrinsic to the compound. A step-by-step discussion of the lattice dynamics would exceed the present space limitations, and therefore, we refer the reader to Brüesch and Bührer,⁶ publications quoted therein, and the (incomplete) list of studies listed here.^{7–15} From the rich literature, most significantly from polarized spectroscopy on single crystals, the relevant points can be summarized as follows: (1) Most authors agree in assigning the strong 500-cm⁻¹ line (undisputedly intrinsic) to the vibration of the bridging oxygen. Its frequency shift upon ¹⁶O-¹⁸O exchange thus strongly indicates a nonpreferential isotope exchange, with ¹⁸O occupancy clearly present at the site under discussion. (2) Also, the line at ≈ 435 cm⁻¹ is unambigu-

ously shown to be intrinsic and not "mostly" due to an alleged impurity phase. (3) The lines above 500 cm⁻¹ (≈ 590 and 640 cm⁻¹) may well coincide with lines of related copper-oxide compounds, including BaCuO₂ as proposed in Ref. 7 and referred to in the Comment, but this is to be expected anyway. Three independent results make it plausible that at least the 590 line is indeed intrinsic and becomes Raman active as a result of local symmetry breaking. (a) Single crystals exhibit polarized scattering up to these frequencies. (b) Phonon lines up to ≈ 650 cm⁻¹ are observed in infrared transmission spectroscopy, which is a bulk probe. (c) Phonon density of states up to ≈ 650 –700 cm⁻¹ is also found in inelastic neutron scattering.⁶

In conclusion, we return to the magnitude of the oxygen isotope effect. Even if the largest claimed T_c variations are considered, the isotope effect is still very small ($\alpha < 0.04$). Most interestingly, we have found for the high- T_c oxide superconductors a systematic decrease of α with increasing T_c ,¹⁶ going from Ba(Pb,Bi)O₃ ($T_c = 11$ K, $\alpha = 0.22 \pm 0.03$) to (La, Sr)₂CuO₄ ($T_c = 36$ K, $\alpha = 0.16 \pm 0.02$) and to the 1-2-3 compounds. This trend of α vs T_c adds a new perspective to the discussion about the isotope effect in these oxide superconductors.

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Received 31 December 1987

PACS numbers: 74.70.Vy, 74.30.Ek

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