

# Correlation between the critical temperature and the vibrational spectra of high- $T_c$ superconductors

A. A. Bush,<sup>1)</sup> I. S. Dubenko,<sup>1)</sup> M. F. Limonov, Yu. F. Markov, A. G. Panfilov, B. S. Razbirin, and O. V. Sokolova<sup>1)</sup>

*Physicotechnical Institute, Academy of Sciences of the USSR*

(Submitted 4 May 1989; resubmitted 31 July 1989)

Pis'ma Zh. Eksp. Teor. Fiz. **50**, No. 5, 250–253 (10 September 1989)

A correlation between the increase in the critical temperature ( $T_c$ ) and the increase in the frequencies of the vibrational spectra of various perovskite-like high- $T_c$  superconductors has been established empirically for the first time. On the basis of this correlation a new system ( $Y_{1-x}Sc_x$ ) ( $Ba_{1-y}Sr_y$ )<sub>2</sub>Cu<sub>3</sub>O<sub>δ</sub> has been synthesized and analyzed. In this system  $T_c$  has been observed to increase at intermediate concentrations.

The mechanism for high- $T_c$  superconductivity so far has not been explained and the role of phonons is now being vigorously discussed. An impression has therefore been created that information on the transition to the superconducting state obtained from vibrational spectroscopy is rather sparse. The principal manifestation of the superconducting transition in a Raman spectrum is the detection of an anomalous behavior of the frequency of a line at  $T < T_c$  in the Raman spectrum of several high- $T_c$  superconducting compounds.<sup>1,2</sup> The use of vibrational spectroscopy in the explanation of high- $T_c$  superconductivity may nonetheless prove to be of greater fundamental importance. In the present letter we confirm the correlation between the critical temperature  $T_c$  and the frequencies of the vibration spectra of several high- $T_c$  superconducting materials and show that this correlation may be evidence of the importance of electron-phonon coupling in the mechanism describing high- $T_c$  superconductivity. The diagram in Fig. 1 shows the frequencies of two Raman spectrum lines of high- $T_c$  superconducting compounds: the line in the  $zz$  polarization, which has the highest frequency in the Raman spectrum,  $\nu_{zz}$ , and the most intense line (and the only one in many cases) in the  $xx$  polarization,  $\nu_{xx}$ . The frequencies were taken from Refs. 3–7. Figure 1 also shows the calculated frequencies  $\nu_c = 2\pi kT_c$ , which are used as a critical temperature frame of reference. In the BCS theory the phonons with frequencies of  $\nu_c$  contribute significantly to  $T_c$  (Ref. 8).

Figure 1 implies that an increase in  $T_c$  on going from one compound to another is accompanied by a corresponding increase in the frequencies  $\nu_{xx}$  and  $\nu_{zz}$  (the latter frequency determines to a large extent the effective frequency of the phonon spectrum). Another intriguing consequence of this conclusion is that  $\nu_c$  in several cases is nearly equal to  $\nu_{xx}$ , the frequency of the line which is polarized in the basal plane (the  $xy$  plane of the CuO<sub>2</sub> layers, whose importance in the high- $T_c$  superconductivity mechanism is obvious).

Assuming on the basis of Fig. 1 that there is a correlation between  $T_c$  and the frequencies of the vibrational spectra of high- $T_c$  superconducting compounds, we can

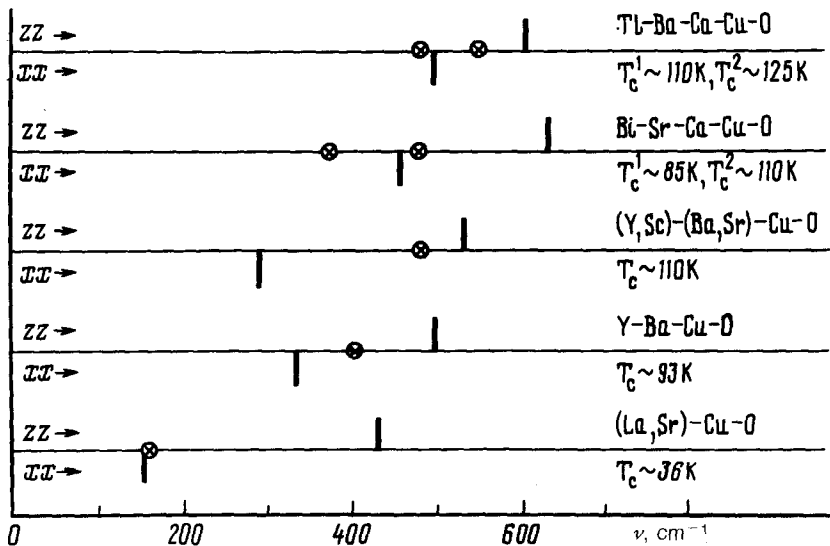


FIG. 1. Characteristic frequencies  $\nu_{xx}$ ,  $\nu_{zz}$ , and  $\nu_c$  ( $\otimes$ ) for high- $T_c$  superconductors. The explanation is given in the text.

combine several widely known experimental results and draw some conclusions on their basis.

1. *Temperature-induced softening of  $\nu_{xx}$  in the Raman spectrum.* At  $T < T_c$  a softening of the  $\nu_{xx}$  line with a frequency  $\sim 335 \text{ cm}^{-1}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$  (Ref. 1) and with a frequency  $463 \text{ cm}^{-1}$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_\gamma$  (Ref. 2), probably due to the electron-phonon coupling, has previously been detected in the Raman spectra. Accordingly, the line considered above,  $\nu_{xx} \sim \nu_c = 2\pi k T_c$ , is the line most sensitive to the superconducting transition. A similar temperature dependence can therefore be expected to apply to  $\nu_{xx} \sim 153 \text{ cm}^{-1}$  in  $(\text{La}, \text{Sr})\text{CuO}_4$  and to  $\nu_{xx} \sim 495 \text{ cm}^{-1}$  in  $\text{Tl}_2\text{Ba}_2\text{Cu}_3\text{O}_\gamma$ .

2. *Dependence of  $T_c$  on pressure.* An increase of  $T_c$  in high-pressure experiments (see Ref. 9, for example) can be attributed to the rf shift of the entire vibrational spectrum. An increase in  $T_c$  was also observed in the case of "intrinsic" strain of a crystal lattice produced by changing the concentration of the unit cell constants, including those of mixed compounds. In a  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$  system, for example, upon an increase in the oxygen concentration from  $\gamma = 6$  to  $\gamma = 7$ , a nontrivial decrease in the value of the parameter  $c$  (Ref. 10) is accompanied by a correlated increase of  $\nu_{zz}$  and  $T_c$  (Ref. 11), although purely electronic effects may also play an important role in this particular case. Since there is no correlation between  $T_c$  and  $c$  in the entire class of high- $T_c$  superconducting compounds, the basic case for a correlation between  $T_c$  and  $\nu$  cannot be based on the fact that they both depend on the lattice constants.

3. *Dependence of  $T_c$  on the systematic features of the structure.* On the basis of Fig. 1 we can assume that the breadth of the photon spectrum characterizes the maximum critical temperature of each compound. An increase in the volume of the provs-

kite-like crystal lattice as a result of adding to it the structural elements which it already contains (in particular, the planes consisting of Ca atoms and the  $\text{CuO}_2$  planes) does not lead to the appearance of fundamental oscillations with frequencies which differ substantially from those already available, and the upper limiting frequency of the vibrational spectrum does not increase appreciably. An increase in the number of  $\text{CuO}_2$  layers in the compounds  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ , for example, with large values of  $n$  ( $n = 4, 5, \dots$ ), therefore does not lead to a substantial increase of  $T_c$ .

4. *Outlook for a further increase of the  $T_c$ .* On the basis of the correlation between  $T_c$  and  $\nu$  it is possible to estimate the expected variation of  $T_c$  in high- $T_c$  superconducting compounds from the vibrational spectra.<sup>2)</sup> Replacement of the components which lead to an increase in the vibrational frequencies (optical and acoustic), i.e., the rigidity of the crystal lattice, holds promise in the quest to increase  $T_c$ . If the relation shown in Fig. 1 is preserved, the vibrational spectrum of the compound with  $T_c \sim 300$  K should be characterized by the frequencies  $\sim 10^3 \text{ cm}^{-1}$ .

5. *A new high- $T_c$  superconducting system  $(\text{Y}_{1-x}\text{Sc}_x)(\text{Ba}_{1-y}\text{Sr}_y)_2\text{Cu}_3\text{O}_\delta$ .* On the basis of the proposed model the following series of isovalent substitutions in the original system La-Ba-Cu-O hold promise:  $\text{La} \rightarrow \text{Y} \rightarrow \text{Sc}$  and  $\text{Ba} \rightarrow \text{Sr} \rightarrow \text{Ca}$ . As a result of such substitutions, the system can break up, because of the considerable difference in the radii of the replaceable atoms, into several immiscible phases. To stabilize the lattice, we have therefore made a double parallel substitution  $(\text{Y}_{1-x}\text{Sc}_x)(\text{Ba}_{1-y}\text{Sr}_y)_2\text{Cu}_3\text{O}_\delta$ . X-ray diffraction studies showed that the samples with the component concentrations  $0 \leq x = y \leq 0.3$  are nearly single-phase samples and that they have a perovskite-like structure of the  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$  type with a deficiency of oxygen whose concentration has not been determined. At  $x, y > 0.3$  the ceramics contain an appreciable number of impurity phases. The samples with the concentrations  $0 \leq x = y < 0.25$  are orthorhombic samples. We have focused our attention principally on the compound  $(\text{Y}_{0.75}\text{Sc}_{0.25})(\text{Ba}_{0.75}\text{Sr}_{0.25})_2\text{Cu}_3\text{O}_\delta$  which has a tetragonal symmetry with the unit cell parameters  $a = b = 3.856(4) \text{ \AA}$  and  $c = 11.575(4) \text{ \AA}$ . Note that the parameter  $c$  of the mixed compound is smaller than that of the parent compound  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$ , whose value is  $c = 11.67 \text{ \AA}$ .

According to the  $\rho(T)$  plots which we measured, the transition to the superconducting state of the samples with a concentration  $x = y = 0.25$  begins at  $T_{c,h} \approx 110 \text{ K}$  and is completed at  $T \approx 80 \text{ K}$ . Upon changing the magnetic susceptibility the deviation from the Curie-Weiss law  $\chi^{-1}(T)$  occurs at  $T \approx 100 \text{ K}$ . The results of the measurement of  $\rho(T)$  and  $\chi(T)$ , taken together, suggest that a superconducting phase forms in the compound  $(\text{Y}_{0.75}\text{Sc}_{0.25})(\text{Ba}_{0.75}\text{Sr}_{0.25})_2\text{Cu}_3\text{O}_\delta$  in the temperature region 100–110 K.

The Raman spectra were investigated using a Z-24 (DILOR) triple Raman spectrometer. The Raman spectra of the samples of  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$  ( $\gamma \sim 7$ ) and of the mixed compound ( $x = y = 0.25$ ) in the region of vibration of the oxygen atoms are shown in Fig. 2. Interpretation of the Raman-spectrum lines of  $\text{YBa}_2\text{Cu}_3\text{O}_\gamma$  is well known.<sup>4,5</sup> In the Raman spectrum of a mixed compound worth noting is the intense line at  $533 \text{ cm}^{-1}$ , which is apparently caused by the introduction of lighter atoms—Sc or Sr—into the original matrix, which accounts for the so-called multimodal behavior

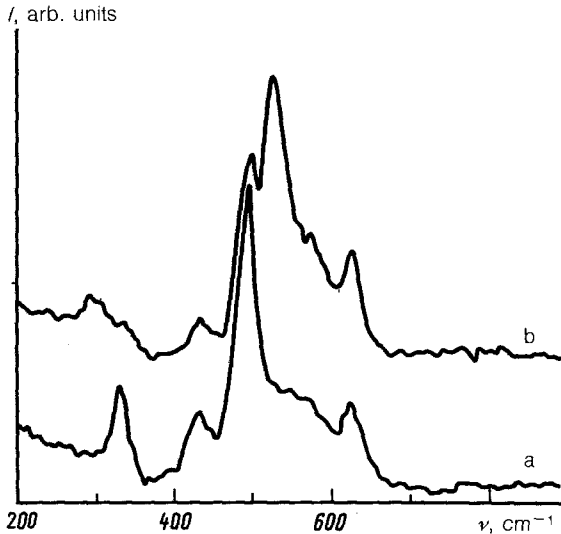


FIG. 2. Raman spectra of the compound (a)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and the compound (b)  $(\text{Y}_{0.75}\text{Sc}_{0.25})(\text{Ba}_{0.75}\text{Sr}_{0.25})_2\text{Cu}_3\text{O}_8$ , measured at room temperature.

of the optical oscillations in the mixed systems.<sup>13</sup> Specifically, the appearance in the phonon spectrum of an oscillation of frequency higher than that in the spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  can account for the increase in the critical temperature ( $T_c$ ) of  $(\text{Y}_{0.75}\text{Sc}_{0.25})(\text{Ba}_{0.75}\text{Sr}_{0.25})_2\text{Cu}_3\text{O}_8$ .

The various pieces of evidence presented above confirm that there is a correlation between the vibrational frequencies and the critical temperature  $T_c$ . This correlation suggests that the electron-phonon coupling is a dominant factor in the high- $T_c$  superconductivity mechanism.

We wish to thank V. S. Vikhnin, Yu. M. Gal'perin, A. A. Kaplyanskii, A. S. Sigov, and V. B. Timofeev for critical comments. We also thank I. O. Grechkov for assistance with the experiments.

<sup>1</sup>Institute of Informatics, MIREA, Moscow

<sup>2</sup>Empirical Mathiessen's rules were formulated for low-temperature superconductors:  $T_c$  increases with decreasing mass of the atom, which is contained in the superconducting compound, and with increasing radius of this atom.<sup>12</sup> Both of these atomic parameters determine the vibration frequencies of the crystal lattice.

<sup>1</sup>R. M. Macfarlane *et al.*, *Solid State Commun.* **63**, 831 (1987).

<sup>2</sup>G. Burns *et al.*, *Phys. Rev. B* **39**, 775 (1989).

<sup>3</sup>Yu. S. Ponosov and G. A. Bolotin, *Pis'ma Zh. Eksp. Teor. Fiz.* **49**, 16' (1989) [*JETP* **49**, 16 (1989)].

<sup>4</sup>A. V. Bazhenov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 162 (1988) [*JETP Lett.* **47**, 198 (1988)].

<sup>5</sup>M. F. Limonov *et al.*, *Pis'ma Zh. Tekh. Fiz.* **14**, 1235 (1988) [*Sov. Tech. Phys. Lett.* **14**, (1988)].

<sup>6</sup>A. A. Bush *et al.*, *SFKhT* **2**, No. 9, (1989), (in press).

<sup>7</sup>L. V. Gasparov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **49**, 58 (1989) [*JETP Lett.* **49**, 68 (1989)].

<sup>8</sup>G. Bergmann and D. Rainer, *Zeitschrift für Physik*, **263**, 59 (1973).

<sup>9</sup>I. V. Berman *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 634 (1988) [*JETP Lett.* **47**, 733 (1988)].

<sup>10</sup>I. V. Aleksandrov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **48**, 449 (1988) [*JETP Lett.* **48**, 493 (1988)].

<sup>11</sup>A. F. Goncharov *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **48**, 453 (1988) [*JETP Lett.* **48**, 497 (1988)].

<sup>12</sup>A. I. Golovashkin and T. I. Kuznetsova, *Trudy FIAN* **151**, 3 (1984).

<sup>13</sup>G. M. Zinger *et al.*, *Fiz. Tekh. Poluprovodn.* **10**, 479 (1976) [*Sov. Phys. Semicond.* **10**, 286 (1976)].

Translated by S. J. Amoretti