New possibilities for studying the phonon spectra of crystals with the perovskite structure

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A study of the anisotropy of the temperature dependence of the sound velocity $c_{\mathbf{n}}$ in the basal plane of crystals of tetragonal symmetry makes possible an unambiguous determination of the energy and nature of the optical phonon mode (soft mode) which is interacting with the sound.

In this letter we wish to demonstrate some new spectroscopic possibilities for studying the phonon spectra of crystals with a soft mode by an acoustic method. We will discuss the particular case of a study of the anisotropy of the temperature dependence of the longitudinal sound velocity, $c_{\mathbf{n}}(T)$, in an La_2CuO_4 single crystal[1] (**n** is the sound propagation direction in the crystal). An unexpected result in Ref. 1 was that the $c_{\mathbf{n}}(T)$ dependence is quite different along the $\mathbf{n} = [100]$ and $\mathbf{n} = [110]$ directions in the basal plane of the crystal. The experimental data of Ref. 1 contradict the standard understanding of the interaction of sound with phonons for crystals with the perovskite structure.[2]

We will show here that the anisotropy observed for $c_{\mathbf{n}}(T)$ (Fig. 1) in the basal plane is a consequence of an interaction of a sound wave with a certain type of phonon mode. Working from the theory for the propagation of sound in crystals, whose fundamentals are given in Ref. 3, we calculated the phonon components of all elements of the elastic tensor λ_{ikem} and the viscosity tensor η_{ikem} of the La_2CuO_4 crystal in the tetragonal phase. The slight orthorhombic nature of the La_2CuO_4 crystal is not important for the physical causes of the anisotropy of the acoustic properties in the basal plane. These tensors were found as functionals of the parameters of the energy spectra of the phonon modes, so it became possible to determine the nature and properties of the phonon mode responsible for the observed effects by comparing theory and experiment.

A quantitative analysis showed that the contribution of the acoustic modes is on the order of $(c_{110} - c_{100})/c_{100}$ and amounts to more than 10% of the measured values (Fig. 1). The anisotropy effects in which we are interested here should accordingly be linked with interactions of sound waves with optical phonons. The optical modes of the La_2CuO_4 crystal form six one-dimensional $(2A_{1g} + 3_{2u} + B_{2u})$ and six doubly degenerate (at $K = 0$) $E(2E_g + 4E_u)$ representations of the D_{2h} group. The phonon energy spectra at small $K \neq 0$ are (one-dimensional)

$$\omega^2(k) = \omega_0^2 + c\gamma_{ik}k_i k_k$$

and (E)

$$\omega^2(k,\mu) = \omega_{0E}^2 + c_E^2 \gamma_{ik}^E(\mathbf{n},\mu) k_i k_k; \ \mathbf{n} = \mathbf{k}/|\mathbf{k}|; \ \mu = \pm 1.$$

They contain the tensors γ_{ik}, γ_{ik}^E, which specify the geometric properties of the constant-energy surfaces $\gamma_{ik} k_i k_k = \text{const}$. The former are isotropic in the basal plane because of the tetragonal symmetry of the crystal. The interactions of sound waves with $(2A_{1g} + 3A_{2g} + B_{2u})$ optical phonons thus do not contribute to the phonon part of the anisotropy parameter of the elastic moduli, $\Delta\lambda = \lambda_{1111} - 2\lambda_{1212} - \lambda_{1122}$.

In order to interpret the experimental data, it became necessary to classify the E modes having two mutually perpendicular polarization vectors in the basal plane in terms of the type of degeneracy lifting, i.e., in terms of the structure of the anisotropic tensors $\gamma_{ik}^E(\mathbf{n},\mu)$. This classification is conveniently carried out in terms of the geometric properties of the cross sections of the constant-energy surfaces in the basal plane. These cross sections are figures with a symmetry of either C_{2v} [$E(D_{2v})$ modes] or D_{2h} [$E(D_{2h})$ modes]. The symmetry axes of the figures for the different values $\mu = \pm 1$ are mutually perpendicular: For the $E(C_{2v})$ modes, they are directed along the diagonals of the base of the unit cell, while for the $E(D_{2h})$ modes they are directed along the sides of the base. The initial symmetry of the crystal is seen in the circumstances that when either of the two figures, which constitute an irreducible pair, is superimposed on the other the result is a figure with tetragonal symmetry. This circumstance leads in particular to a tetragonal symmetry of the resultant (over $\mu = \pm 1$) contributions of E modes to the elastic-modulus and viscosity tensors.

For the quantity measured experimentally (Fig. 1), the theory yields the expression

$$A(T) = \frac{c_{100}(T) - c_{100}(0)}{c_{100}(0)} - \frac{c_{110}(T) - c_{110}(0)}{c_{110}(0)} = A_1(T) + A_2(T),$$

$$\left.\begin{aligned} A_1(T) &= \frac{c_{110}^2(0) - c_{100}^2(0)}{2\rho c_{110}^2(0) c_{100}^2(0)} [\lambda_{1111}^{(1)}(T) + \lambda_{1111}^{(2)}(T)], \\ A_2(T) &= \frac{1}{4\rho c_{110}^2(0)} [\lambda_{1111}^{(2)}(T) - 2\lambda_{1212}^{(2)}(T) - \lambda_{1122}^{(2)}(T)], \end{aligned}\right\} \quad (2)$$

where ρ is the density of the crystal, $\lambda_{ikem}^{(1)}(T)$ are the acoustic and optical phonon contributions, which have a weak effect on the anisotropy in the symmetry plane, and $\lambda_{ikem}^{(2)}(T)$ are the contributions of the E modes which are responsible for this anisotropy. The first term in (2) is quantitatively small, on the order of the parameter $(c_{110} - c_{100})/c_{110}$. This circumstance makes it possible to unambiguously establish both the nature of the E mode responsible for the observed macroscopic anisotropy and the temperature dependence of the parameters of its energy spectrum, by comparing theory with experiment. Specifically, the predominant orientation of the wave vectors of the $E(C_{2v})$ modes leads to an additional softening of the crystal along the

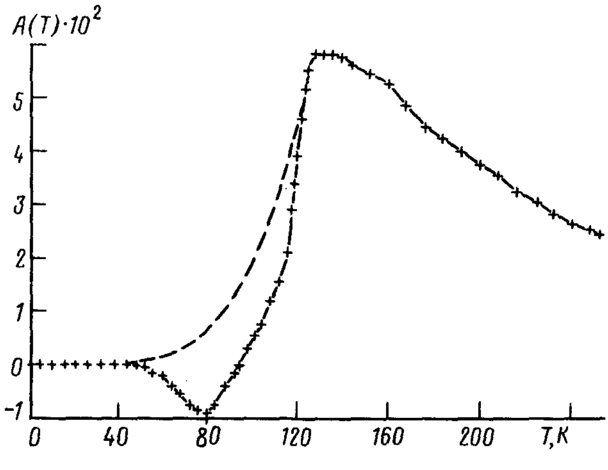

FIG. 1. Temperature dependence of the anisotropy of the sound velocities, $A(T)$, in the basal plane of the La_2CuO_4 crystal. The dashed line shows the function $A_2(T)$ with $c_E = 3.18\times 10^4\sigma(T)^{2/3}$ cm/s, $\rho = 6.4$ g/cm^3, $c_{110} = 5\times 10^5$ cm/s, and $\omega_0 = 124$ K.

diagonals of the base of the unit cell. With $c_{110}\approx c_{100}$ and $T > \hbar\omega_{0E}$, the magnitude of the anisotropy thus satisfies $A(T) > 0$. If the anisotropy results from an interaction of sound waves with $E(D_{2h})$ phonons, on the other hand, we have $A(T) < 0$.

At $c_{110}\approx c_{100}$, the sign at $A(T)$ is thus a reliable indicator of the nature of the waves which generate the soft mode. The eigenfrequency of this mode can be estimated from the position along the temperature axis of the region in which the function $A(T)$ rises steeply.

The experiments single out the $E(C_{2v})$ mode. In the calculation of $A(T)$, it is sufficient to approximate the cross sections of its constant-energy surfaces in the basal plane by effective ellipses whose major axes are oriented along the diagonals of the base of the cell. In this case the tensor $\gamma_{ik}(E,\mathbf{n},\mu)$, which appears in phonon spectra (1), has the simple form

$$\gamma_{11}(\mu) = \gamma_{22}(\mu) = \sqrt{1+\sigma^2(T)};\quad \gamma_{12}(\mu) = \gamma_{21}(\mu) = \mu\sigma(T);\ \mu = \pm 1, \tag{3}$$

where $\sigma(T)$ is the difference between the semiaxes of the effective ellipse. For the contribution of the E_μ modes to the elastic-modulus tensor we find the expression

$$\lambda^{(2)}_{ikem} = \sum_{E,\mu}[\gamma_{im}(E,\mu)\gamma_{ke}(E,\mu) + \gamma_{ie}(E,\mu)\gamma_{km}(E,\mu)]$$
$$\times \int \frac{d^3k}{(2\pi)^3}\Big[\frac{c_E^2\gamma_{pq}(E,\mu)k_pk_q}{3\omega_{E\mu}^2}n\Big(\frac{\hbar\omega_{E\mu}}{T}\Big)$$
$$+\frac{c_E^4(\gamma_{pq}(E,\mu)k_pk_q)^2}{\omega_{E\mu}^4}\frac{\hbar\omega_{E\mu}}{T}n'\Big(\frac{\hbar\omega_{E\mu}}{T}\Big), \tag{4}$$

where $n(\hbar\omega_{E\mu}/T)$ is a Bose-Einstein distribution, and $n'(\hbar\omega_{E\mu}/T)$ is its derivative with respect to the variable $\hbar\omega_{E\mu}/T$. The expression for $\lambda^{(1)}_{ikem}$ is far more complicated; it contains, in contrast with the expression for $\lambda^{(2)}_{ikem}$, not only the parameters of spectra (1) themselves but also their derivatives with respect to the temperature and the density.

Calculating the function $A_2(T)$ with the help of (3) and (4), we find

$$A_2(T) = \frac{\pi^2}{225}\frac{\sigma^2(T)T^4}{(\hbar c_E)^3\rho c_{110}^2} B\left(\frac{\hbar\omega_{0E}}{T}\right),$$

$$B\left(\frac{\hbar\omega_{0E}}{T}\right) = B(x) = \frac{15}{\pi^4}\int_0^\infty \frac{z^6 dz}{(z^2+x^2)^{3/2}[\exp(z^2+x^2)^{1/2}-1]}. \quad (5)$$

In the region $T < \hbar\omega_{0E}$, $\sigma(T) = \text{const}$, we find

$$B\left(\frac{\hbar\omega_{0E}}{T}\right) = \frac{225}{\pi^{7/2}\sqrt{2}}\left(\frac{\hbar\omega_{0E}}{T}\right)^{1/2}\exp\left(-\frac{\hbar\omega_{0E}}{T}\right). \quad (6)$$

According to (5) and (6), the interval $[0, h\omega_{0E}]$ is the region of the steep rise of the function $A(T)$. At $T > \hbar\omega_{0E}$, the function $\sigma(T)$ is a decreasing function of the temperature, so the energy spectrum of the soft mode is isotropic $[B(x)\to 1]$. It follows that the eigenfrequency of the soft mode can be determined reliably from the position of the peak on the $A(T)$ curve; $\hbar\omega_{0E} \approx 11$ meV. The existence of a mode with such an eigenfrequency is supported by independent experiments.[4,5]

The dashed line in Fig. 1 shows the function $A_2(T)$ calculated from (5) in the region $T \leqslant \hbar\omega_{0E}$. The difference between the experimental curve of $A(T)$ and $A_2(T)$ is a consequence of the function $A_1(T)$, given in (2). The theoretical expression for $A_1(T)$, which we are not reproducing here because of its length, makes it possible to explain both the sign of $A_1(T) < 0$ and the magnitude of this function.

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