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Anharmonic decay of optical phonon in diamond*

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(Received 2 January 1975)

The width of the 1332-cm^{-1} first-order Raman line in diamond, measured by Krishnan and by Solin and Ramdas from 15 to 970 K, varies with temperature as expected from the anharmonic interaction of the optical phonon with two phonons of half the frequency. The magnitude of the width agrees with a theoretical estimate by Klemens.

Owing to the cubic anharmonicity of the crystal forces, the $\vec{k}=0$ optical phonon can decay spontaneously into two acoustical phonons of equal and opposite momentum. This interaction contributes to the width of the optical-phonon line in the first-order Raman spectrum. The interaction rate is enhanced with increasing temperature by the prior excitation of the participating acoustical modes. An estimate of the linewidth at zero temperature has been made, and an exact expression has been given for its temperature dependence.[1] This result was compared to the Raman linewidth of the optical mode of silicon at room temperature observed by Parker, Feldman, and Ashkin.[2] The agreement was reasonably good, considering the simplifications made in this theory.

Solin and Ramdas[3] have since studied the Raman spectrum of diamond at low temperatures, and in particular, they measured the width of the first-order Raman line at 1332 cm^{-1}, ascribed to the LO mode at $\vec{k}=0$, in the temperature range of 15–300 K. Their results link up well with earlier measurements by Krishnan[4] over the temperature range of 300–970 K. The purpose of this note is to point out that the temperature dependence of the linewidth agrees well with that required by theory, so that the anharmonic decay of the optical phonon into two acoustic phonons seems to be indeed the dominant broadening mechanism. Also, the absolute magnitude of the zero-temperature linewidth seems to be in fair agreement with the theoretical estimate.

The half-width at half-intensity of the Raman line, expressed in radian/(unit time), may be identified with the phonon relaxation rate, as defined in Ref. 1. The latter has the form

$$1/\tau(T)=A[1+2N(\tfrac{1}{2}\omega_0)], \tag{1}$$

where ω_0 is the optical-mode frequency, $N(\frac{1}{2}\omega_0)$ is the average number of phonons in a lattice mode of frequency $\frac{1}{2}\omega_0$ at temperature T, and A is the relaxation rate at $T=0$, to be discussed below. The temperature dependence of Eq. (1) is based on the assumption that the major decay process is the anharmonic interaction of the optical phonon with two acoustic phonons, each of half the frequency and of opposite wavevectors. This temperature dependence should thus be well obeyed, even if the theory can only approximate the value of A.

Solin and Ramdas[3] found $1/\tau$ to be 1.48 ± 0.02 cm^{-1}. Krishnan[4] obtained a slightly higher value, 1.7 cm^{-1}, at 300 K (but his instrumental width was larger), and he found the width to increase further with temperature, reaching 3.3 cm^{-1} at 970 K. Taking A to be 1.48 cm^{-1}, $1/\tau$ from Eq. (1) should be 1.61 cm^{-1} at 300 K and 3.26 cm^{-1} at 970 K. Hence the temperature dependence of $1/\tau$ seems to obey (1) to within experimental accuracy, and the broadening mechanism appears indeed to be the anharmonic decay of the LO phonon into two phonons, each of half the frequency.

The coefficient A in Eq. (1) is given by[1]

$$A=\frac{2.5\gamma^2}{\pi}\,\omega_0\frac{h\omega_0}{Mv^2}\left[\frac{4}{3}\left(\frac{\alpha-\beta}{\alpha+\beta}\right)^2\right], \tag{2}$$

where M is the atomic mass; v is the velocity of the acoustic phonons; and γ, the Grüneisen constant, is a measure of the anharmonicity.

The factor in large square brackets arises because the strain field of the optical mode differs from that of an acoustic mode. It describes the change in the frequencies of the acoustic waves due to the displacement field of the optical mode, using the simplified model of a linear chain of identical atoms with anharmonic linkages of alternating force constants. The ratio α/β is then equated to the square of the ratio of the optical and acoustic mode frequencies at the zone boundary. From the dispersion curves of Warren *et al.*[5] it appears that $\alpha/\beta = 1.4$. With $\gamma = 2$, $Mv^2/k = 2.5\times10^5$ K, and $h\omega_0/k = 1933$ K, one obtains from (2) that $A = 1.2$ cm^{-1}. The value found by Solin and Ramdas[3] is 1.48 cm^{-1}. Considering the approximations of the theory and the uncertainties of the parameters entering (2), this is satisfactory agreement.

The author acknowledges discussions with Professor A. K. Ramdas, made possible by the hospitality of the Thermophysical Properties Research Center of Purdue University.

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*Supported by the U. S. Army Research Office, Durham, N. C.

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