

the center, the period increases to more than twice its normal value. After the off-center oscillations begin, the period decreases rapidly to less than its original value.

The apparatus is not such as to permit highly quantitative description of the results, but two conclusions seem to be justified: (1) The conservative force is apparently associated with currents in the film at the boundary between normal and superconducting areas. (2) The dissipative force cannot be due to ordinary eddy currents since it is not observed at 4.2°. The resistance of the film in the nor-

mal state is high enough, because of its small thickness, to make this contribution negligible. The force must be associated with the motion of normal superconducting boundaries.

<sup>1</sup>C. F. Hempstead and Y. B. Kim, Phys. Rev. Letters **12**, 145 (1964).

<sup>2</sup>Ivar Giaever, Phys. Rev. Letters **15**, 825 (1965).

<sup>3</sup>P. R. Solomon, Phys. Rev. Letters **16**, 50 (1965).

<sup>4</sup>Judea Pearl, Phys. Rev. Letters **16**, 99 (1965).

<sup>5</sup>W. V. Houston and C. F. Squire, Phys. Rev. **76**, 685 (1949).

### ANOMALOUS STRESS EFFECTS IN RESONANT-MODE INFRARED ABSORPTION\*

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In this paper we report about the anomalous behavior that the resonant-mode infrared absorption exhibits under the application of uniaxial or hydrostatic stress. The main feature of the effect consists in the large shift that the peak frequency suffers under the application of the stress. Indeed this shift is predicted to be in some cases 20 times larger than the shift suffered by the host lattice frequencies.

In the absence of any concentration effect, it is well known<sup>1-3</sup> that the absorption peak occurs at the frequency for which the real part of the resonance denominator of the scattering matrix for a single imperfection vanishes. If, in addition to the change of mass, the change of nearest-neighbor (n.n.) force constant is also considered, it is an easy matter to generalize the theoretical results of previous authors<sup>1,3</sup> concerning the pure change of mass, and the resonant frequency  $\omega_r$  for the optically active mode turns out to be a root of the equation

$$1 + \epsilon\alpha(\omega_r) + \bar{\lambda}\beta(\omega_r) + \epsilon\bar{\lambda}\gamma(\omega_r) = 0. \quad (1)$$

$\epsilon = \Delta M_{\pm}/M_{\pm}$  measures the local change in mass,  $\lambda \equiv M_{\pm}\bar{\lambda}$  the local change in nn force constant of central type, while  $\alpha(\omega)$ ,  $\beta(\omega)$ , and  $\gamma(\omega)$  denote the real part of Brillouin-zone summation involving the frequencies and the polarization vectors of the host crystal. In an ionic crystal with rock-salt structure,  $\alpha(\omega)$ ,  $\beta(\omega)$ , and  $\gamma(\omega)$

turn out to be

$$\alpha(\omega) = \omega^2 \operatorname{Re} \mathcal{G}_1(\omega),$$

$$\beta(\omega) = \operatorname{Re} \{ \mathcal{G}_1(\omega) - 2\chi^{1/2} \mathcal{G}_2(\omega) + \chi \mathcal{G}_3(\omega) \}$$

$$\gamma(\omega) = \omega^2 \chi \operatorname{Re} \{ \mathcal{G}_1(\omega) \mathcal{G}_3(\omega) - \mathcal{G}_2^2(\omega) \};$$

$$\mathcal{G}_1(\omega) = N^{-1} \sum_{\vec{q}j} (\omega_{\vec{q}j}^2 - \omega^2 - 2i\omega 0^+)^{-1} e_x^2(\pm|\vec{q}j),$$

$$\mathcal{G}_2(\omega) = N^{-1} \sum_{\vec{q}j} (\omega_{\vec{q}j}^2 - \omega^2 - 2i\omega 0^+)^{-1} e_x(\pm|\vec{q}j)$$

$$\times e_x(\mp|\vec{q}j) \cos(2\pi a q_x),$$

$$\mathcal{G}_3(\omega) = N^{-1} \sum_{\vec{q}j} (\omega_{\vec{q}j}^2 - \omega^2 - 2i\omega 0^+)^{-1}$$

$$\times e_x^2(\mp|\vec{q}j) \cos^2(2\pi a q_x). \quad (2)$$

In the above expression,  $\omega$  is the circular frequency,  $\vec{q}$  the wave vector,  $j$  the branch index,  $n$  the number of primitive cells comprising the lattice, and  $a$  the lattice constant.  $\vec{e}(\pm|\vec{q}j)$  is the polarization vector of positive (+) or negative (-) ions and  $\chi = M_{\pm}/M_{\mp}$  the host-crystal mass ratio; the choice of the upper or lower sign depends whether we are concerned with positive or negative impurities.

For a fixed value of the resonant frequency,

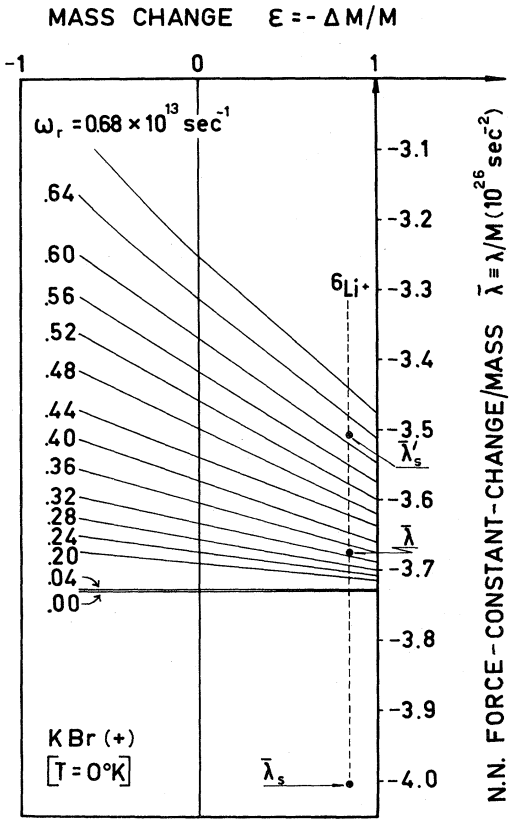


FIG. 1. The resonances frequency as a function of the changes of mass  $\epsilon$  and force constant  $\bar{\lambda}$ ; for positive impurities in a KBr crystal at 0°K.

Eq. (1) represents a hyperbola in the  $(\epsilon, \bar{\lambda})$  plane. The hyperbola represents all the possible pairs of  $\epsilon$  and  $\bar{\lambda}$  values for which a resonance occurs at the considered frequency. Figure 1 shows the hyperbolas for a KBr host lattice which correspond to positive impurities and to a set of frequencies uniformly distributed in the acoustic region.

The coefficients  $\alpha(\omega)$ ,  $\beta(\omega)$ , and  $\gamma(\omega)$  were evaluated by using Hardy's deformation dipole model,<sup>4</sup> zero-temperature crystal data,<sup>5</sup> and a grid of 4409 points in the Brillouin zone.

From Fig. 1 it appears that the smaller the resonance frequency, the more the hyperbolas approach one to another. This occurs particularly in the region of the  $(\epsilon, \bar{\lambda})$  plane which corresponds to light substitutional impurities. The plot in Fig. 1 accounts qualitatively for the high sensitivity that the resonance frequency may exhibit to a variation of the change of force constant. Indeed it appears that for  $\epsilon(^6\text{Li}^+)$

= 0.847, a very small variation of  $\bar{\lambda}$  gives rise to a very large change of the resonant frequency or even the disappearance of the resonance itself.

An external stress, a strong electric field, or a change in temperature, all are methods to produce a variation of  $\bar{\lambda}$ . These external perturbations affect also the lattice dynamics; we have considered the simplest one, i.e., a hydrostatic pressure. Use is made of the Grüneisen approximation, i.e.,

$$\omega_{s, \vec{q}j}^2 = \omega_{\vec{q}j}^2 \{1 - 6\gamma da/a\} \quad (3)$$

for all  $\vec{q}$  and  $j$ . A subscript  $s$  is added to quantities in stressed crystals and  $\gamma$  is the average of the "mode-gammas."<sup>6</sup> It is easy to show that under hydrostatic stress the absorption coefficient transforms as

$$\alpha_s(\omega; \bar{\lambda}) = \{1 + 3\bar{\gamma} da/a\} \alpha(\omega'; \bar{\lambda}_s'), \quad (4)$$

where

$$\omega' = \omega \{1 + 3\gamma da/a\}, \quad \bar{\lambda}_s' = \bar{\lambda} \{1 + 6\gamma da/a\}, \quad (5)$$

and  $\bar{\gamma} = \gamma + \gamma_{\text{LO}} - \gamma_{\text{TO}} - 1$  is the amplitude factor. If the impurity n.n. force constant would change under stress as much as the n.n. force constant of the host lattice,  $\bar{\lambda}$  would transform as a squared normal frequency, i.e.,  $\bar{\lambda}_s = \bar{\lambda} (1 - 6\gamma da/a)$ ; in this case  $\bar{\lambda}_s' = \bar{\lambda}$ , and it appears from Eq. (4) that the resonance frequency would shift as much as the normal-mode frequencies. As a matter of fact  $\bar{\lambda}_s'$  differs from  $\bar{\lambda}$ ; this accounts for the anomalous stress effect.

For KBr the average "mode-gamma" was estimated to be  $\gamma = 2.12$ . The sharp resonance<sup>7</sup> at  $\omega_r = 0.33 \times 10^{13} \text{ sec}^{-1}$  due to  $^6\text{Li}^+$  in KBr was considered. In the unstressed crystal the resonance peak can be fitted by choosing  $\bar{\lambda} = -3.675 \times 10^{26} \text{ sec}^{-2}$  (see Fig. 1). The variation of  $\bar{\lambda}$  due to 1% isotropic strain was evaluated on the basis of a Born-Mayer model for the repulsive potential. The correction due to the n.n. elastic relaxation was considered also; indeed the elastic relaxation is estimated to be -5.4% of the lattice constant.<sup>8</sup> It was found that  $\bar{\lambda}_s = -4.018 \times 10^{26} \text{ sec}^{-2}$  and  $\bar{\lambda}_s' = -3.508 \times 10^{26} \text{ sec}^{-2}$ , so a shift of resonance frequency of the order of 100% is predicted on the basis of the plot in Fig. 1, against the 6% Grüneisen shift. The value of the hydrostatic coefficient, which is here defined by<sup>9</sup>

$$A(S_{11} + 2S_{12}) = \frac{1}{9} \frac{d\omega}{da/a}^k, \quad (6)$$

Table I: Hydrostatic coefficient  $A(S_{11} + 2S_{12})$  at 0°K for some resonant modes.

Crystal	Resonant frequency $\omega_\gamma$ ( $10^{13}$ sec $^{-1}$ )	Average mode gamma $\gamma$	Compressibility $\kappa$ (0°K) ( $10^{-12}$ dyn $^{-1}$ )	Hydrostatic coefficient $A(S_{11} + 2S_{12})$ [cm $^{-1}$ /(kg/mm $^2$ )]
KBr:Li	0.33	2.12	6.17	-0.12
KBr:Ag	0.63	2.12	6.17	-0.04
KCl:Ag	0.72	2.2 <sup>a</sup>	5.26	-0.04
KI:Ag	0.33	2.1	7.75	-0.06
KI:Tl	1.23	2.1	7.75	-0.03
NaCl:Cu	0.38	2.7 <sup>a</sup>	3.98	-0.09
NaCl:Ag	0.97	2.7 <sup>a</sup>	3.98	-0.05

<sup>a</sup>See Ref. 6.

where  $\kappa$  is compressibility and  $S_{ij}$  stiffness constants, is reported in Table I. It seems to agree with the result  $A(S_{11} + 2S_{12}) = -0.18 \pm 0.03$  cm $^{-1}$ /(kg/mm $^2$ ) of a recent experiment by Nolt and Sievers.<sup>10</sup>

Estimations for some doped crystals are also reported in Table I. The theoretical evaluation of the axial and trigonal coefficients is in progress.

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<sup>1</sup>A. A. Maradudin, in Astrophysics and the Many-Body Problem: Brandeis Summer Institute Lectures in The-

oretical Physics, edited by K. W. Ford (W. A. Benjamin, Inc., New York, 1963), Vol. 2, pp. 170-320.

<sup>2</sup>G. Benedek and G. F. Nardelli in Color Centers in Alkali Halides, International Symposium, Urbana, Illinois 1965 (to be published).

<sup>3</sup>P. G. Dawber and R. G. Elliott, Proc. Phys. Soc. (London) **273**, 222 (1963).

<sup>4</sup>J. R. Hardy, Phil. Mag. **7**, 315 (1962).

<sup>5</sup>A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

<sup>6</sup>W. B. Daniels in Lattice Dynamics: Proceedings of the International Conference, Copenhagen, 1963, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1964).

<sup>7</sup>A. J. Sievers and S. Takeno, Phys. Rev. **140**, A1030 (1965).

<sup>8</sup>Y. Fukai, J. Phys. Soc. Japan **18**, 1413 (1963).

<sup>9</sup>W. Gebhardt and K. Maier, Phys. Status Solidi **8**, 303 (1965); see also W. Hayes, H. F. Macdonald, and R. J. Elliott, Phys. Rev. Letters **15**, 961 (1965).

<sup>10</sup>I. G. Nolt and A. J. Sievers, to be published.