We use the experimental value, $d\ln m^*(\zeta)/dP \geq 0.11/$ kbar (this result will be discussed in a subsequent paper) and the free-electron value for $dP/d\zeta$.

[13]In all this discussion we ignore the important effects of breakdown on the amplitude of the dHvA oscillations.

LOCAL-MODE RESONANCE – AN OPTICAL ANALOG OF MÖSSBAUER EFFECT*

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Following a suggestion of Silsbee and Fitchen,[1] the theory of Mössbauer effect is applied to the resonance absorption of light by impurity-induced local modes. The resonance treated as modulation of the local mode by the host-lattice phonons predicts the temperature dependence of peak position, half-width, and intensity of the absorption.

To establish the analogy we consider the resonating system as consisting of two parts, the impurity center and the surrounding lattice. The width of the impurity local mode is determined mainly by the probability of decay of a local mode into crystal modes, and depends on the extent of coupling between the two. The infrared absorption by local mode, especially in the case of light substitutional impurities, is known to consist of a sharp line at low temperatures, and its intensity and width depend strongly on temperature.[2] Only a limited amount of multiphonon structure associated with the main resonance has been observed.[3] The local-mode resonance can therefore be regarded as belonging to a weak- to intermediate-coupling situation with a relatively large f (recoilless fraction of Mössbauer effect). The main resonance may therefore, for the purpose of analogy, be termed a zero-lattice-phonon line.

The local mode or the zero-lattice-phonon line is known to be approximated by an Einstein oscillator,[4] whereas the host lattice will have a complete frequency spectrum of its own, albeit slightly perturbed by the presence of the impurity. In the case of non-Bravais lattices, the lattice phonons will belong to optic and acoustic branches. The Raman-like scattering of the local-mode phonon by the lattice phonons will be controlled by the requirements of momentum and energy conservation. For such a model of the local-mode resonance absorption, one may directly use the expressions developed by McCumber[5] (from the consideration of local lattice distortion in the neighborhood of the impurity) for the shift and width of zero-phonon lines in vibronic spectra. In the Debye approximation for the host-lattice phonons, with a Debye characteristic temperature Θ chosen above the acoustic band but not exceeding the temperature corresponding to the maximum optic frequency, the shift and width of the zero-lattice-phonon lines are given by[6]

$$\Delta\omega(T) = \omega(T) - \omega(0) = \alpha\left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}\,dx \quad (1)$$

and

$$\Gamma(T) = \Gamma(0) + \beta\left(\frac{T}{\Theta}\right)^7 \int_0^{\Theta/T} \frac{x^6 e^x}{(e^x - 1)^2}\,dx. \quad (2)$$

The constants α and β are associated with the scattering of phonons by the local mode and contain the unknown coupling factor.

The expression (1) for the shift of the peak position is the same, apart from a multiplicative constant, as that for the total heat. Thus a correlation between $\Delta\omega(T)$ and the total heat of the host crystal is expected. Such a correlation is shown in Fig. 1 for the local-mode absorption in NaCl:H^-, KCl:H^-, KBr:H^-, and CaF_2:H^-. For CaF_2:H^- the first harmonic of the local mode is also infrared-active, and a correlation with the total heat is possible in this case also.

For the correlation of the half-width with temperature, the residual width is obtained from the extrapolation of low-temperature data to 0°K. The integral of Eq. (2) is done numerically with assumed Debye temperature to give the best fit. Θ obtained in such a fashion was slightly smaller than the calorimetric value but close to the temperature corresponding to the optic phonons. The calculated and observed half-widths are compared in Fig. 2.

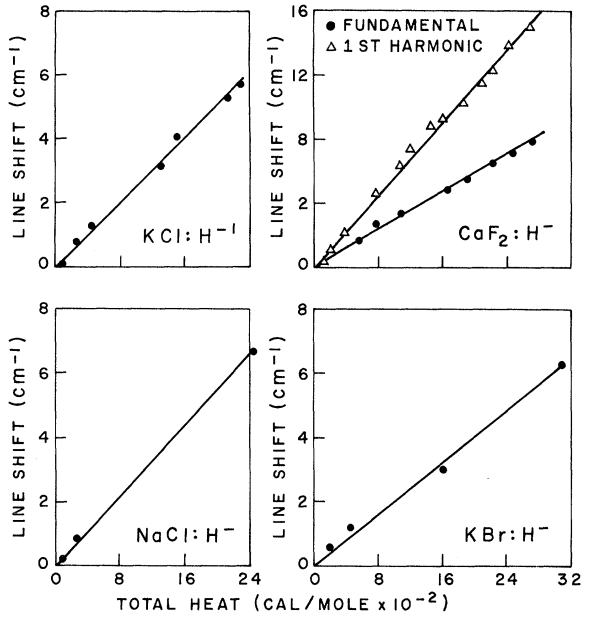

FIG. 1. Shift in local-mode peak position versus total heat. Line-shift data: KCl:H^- from our measurements; NaCl:H^- and KBr:H^- from G. Schaefer, Phys. Chem. Solids 12, 233 (1960); CaF_2:H^- from W. Hayes, G. D. Jones, H. F. Macdonald, C. T. Sennett, and R. J. Elliott, to be published. Heat capacity data: KCl and KBr from W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A242, 467 (1957); NaCl from T. H. K. Barron, A. J. Leadbetter, and J. A. Morrison, Proc. Roy. Soc. (London) A279, 62 (1964); CaF_2 from S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949), and D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).

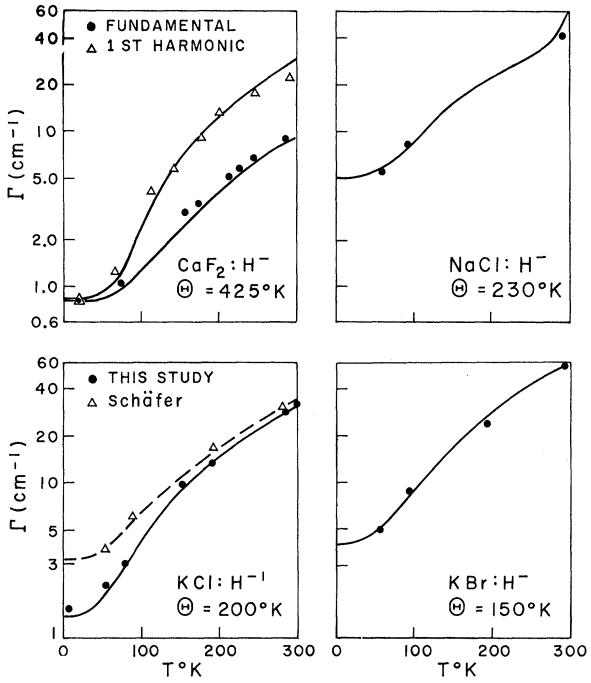

FIG. 2. Temperature dependence of U-center local-mode half-width in several host lattices. Lines are calculated curves with assumed Debye temperatures to give best fit with the experimental data (points). For sources of data see Fig. 1.

It may be noted that at high- and low-temperature limits ($T \gg \Theta$ and $T \ll \Theta$), the temperature-dependent portion of Eq. (2) becomes proportional to T^2 and T^7, respectively. The T^2 dependence of the half-width at high temperatures has been already noted by Mirlin and Reshina[7] in the local-mode resonance of U centers.

In the Debye approximation the theory of the Mössbauer effect[8] predicts that the fraction of transitions without change in the host-lattice states is given by

$$f = e^{-2w}, \tag{3}$$

where the Debye-Waller factor w is given by

$$w = \frac{3R}{k\Theta}\left[\frac{1}{4} + \left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} \frac{x\,dx}{e^x - 1}\right]. \tag{4}$$

Fitchen, Silsbee, Fulton, and Wolf[9] have used Eq. (4) successfully in the case of zero-phonon transitions of color centers in alkali halides. Equations (3) and (4) may be rewritten in a more convenient form:

$$\frac{I_L}{I_B} = \exp -S\left[1 + 4\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} \frac{x\,dx}{e^x - 1}\right]$$

$$\simeq \exp -S[1 + 6.6(T/\Theta)^2] \text{ for } T \ll \Theta, \tag{5}$$

where I_L represents the integrated intensity under the pure (zero-lattice-phonon) local-mode band whereas I_B represents the total band intensity including the multiphonon structure. The factor S in Eq. (5), known as the Huang-Rhys factor, may be identified with the most probable number of phonons involved in the transition, which in the absence of any coupling between the local mode and the lattice phonons should be equal to zero. In the other extreme, for very strong coupling, e.g., the F band, S can be as high as 30.

The total integrated intensity I_B is expected to be independent of temperature. It consists of the local-mode absorption, the difference

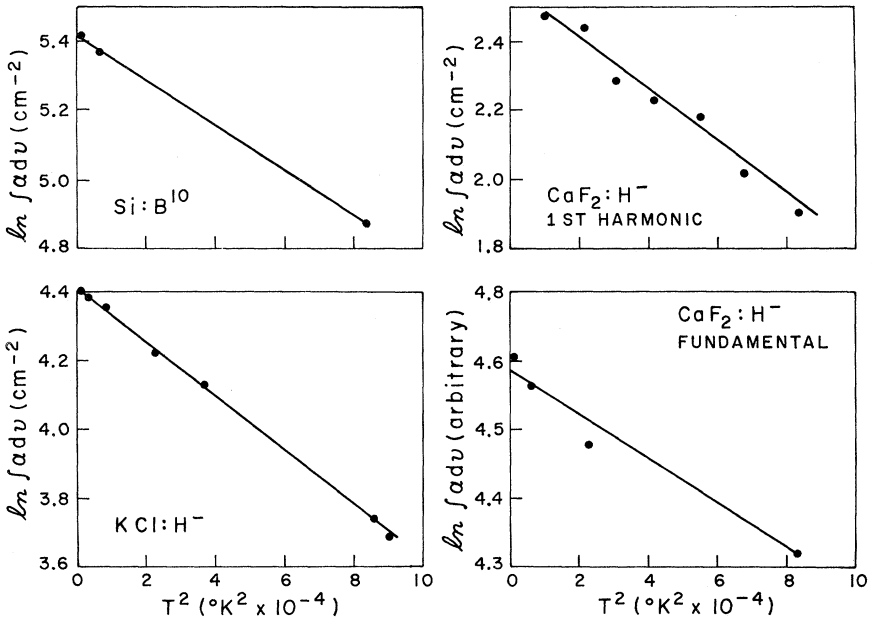

FIG. 3. Temperature dependence of integrated intensity under the local-mode band. Data: Si:B^{10} (681-cm^{-1} band) from M. Balkanski and W. Nazarewicz, to be published; KCl:H^- from our measurements; CaF_2:H^- from W. Hayes, G. D. Jones, H. F. Macdonald, C. T. Sennett, and R. J. Elliott, to be published.

bands, and the sum bands. The absorption coefficient of the high-frequency sum bands has a slight temperature dependence, but that of the low-frequency difference bands has a strong temperature dependence, vanishing completely at very low temperatures. The change in the sideband intensities thus produces a compensating change in integrated intensity of the local mode. The population of the vibrational ground (zero-lattice-phonon) state increases with decreasing temperature and increases the local-mode intensity. Thus, at very low temperatures

$$I_B = I_L + I_{\text{sum}}, \tag{6}$$

and the factor S can be calculated from

$$S = \ln(1 + I_{\text{sum}}/I_L), \tag{7}$$

where I_{sum} indicates the integrated intensity under the sum bands.

In Fig. 3 are plotted $\ln I_L$ vs T^2 for several impurity-host-lattice systems. As predicted by Eq. (5), linear dependence is indeed obtained. The U-center (H^-) local mode in KCl was remeasured at 6°K. The value of S determined from Eq. (7) is 0.052, while that from the slope of the linear plot for this system (Fig. 3) using the value of Θ obtained from the dependence of half-width on T is 0.048, in remarkably good agreement. The low value of S is indicative of relatively weak coupling between the local mode and the lattice modes.

While our work was in progress, Takeno and Sievers[10] in a preprint have pointed out the T^2 dependence of the logarithm of the integrated intensity under the local mode. They, however, did not discuss the various parameters involved in Eq. (5).

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