principle the effect noted here should exist.

The authors wishes to acknowledge valuable discussions with Professor Griffiths, Dr. Teaney, and Dr. Hiroshi Sato.

[1]R. B. Griffiths, private communication.

[2]B. J. C. van der Hoeven, Jr., D. T. Teaney, and V. L. Moruzzi, Bull. Am. Phys. Soc. 13, 163 (1968), D. T. Teaney, B. J. C. van der Hoeven, and V. L. Moruzzi, Phys. Rev. Letters 20, 722 (1968).

[3]S. Shtrikman and D. Treves, in Magnetism, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1963), Vol. III, Chap. 8.

FAR-INFRARED ABSORPTION INDUCED BY ISOTOPES IN NaCl AND LiF †

Miles V. Klein and H. F. Macdonald

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 18 March 1968)

We have made measurements of the far-infrared absorption at 7°K in NaCl. The natural Cl^{35} and Cl^{37} isotopes acting as simple mass defects result in absorption in the acoustic band and yield information about phonon frequencies at critical points. The theory of this effect is derived and applied to NaCl. Similar measurements on LiF are also reported. We believe this to be the first observation of isotope-induced band-mode absorption in alkali halides.

In a large, perfect, harmonic, alkali-halide crystal infrared radiation is absorbed only by the transverse-optic phonon of essentially zero wave vector. This is the only mode of the crystal driven by the long-wavelength external radiation field. Since it is an eigenstate, there is a delta-function response at its frequency ω_0. When monovalent impurities are introduced substitutionally into the crystal, the radiation still drives only the $k \approx 0$, TO mode, but it is no longer an eigenstate. In addition to the delta function at ω_0, absorption appears in the band-mode region, and localized modes may sometimes appear.

The resulting in-band absorption in the acoustical region may be classified into two general types: (1) resonances due to strongly perturbing impurities[1-4] and (2) continuous absorption which reveals critical points in the phonon spectrum. We have given a preliminary report of such continuous spectra for NaCl doped with silver and other monovalent impurities, most of which were strongly coupled.[5] We were able to fit the data fairly well with theoretical calculations using shell-model phonons of Caldwell and Klein[6] after adjusting force-constant changes. However, the calculated peaks in the LA(X) and TA(L) critical-point region were about 6% too low; thus the shell-model parameters used probably gave the wrong phonon frequencies. Since the shape of absorption curves near critical points can be radically changed by strongly interacting impurities, a better test of the phonon model is obtained if

the phonons are merely weakly perturbed. The best weak perturbation is provided by isotopes, since the perturbed dynamical matrix is then known exactly with no force-constant changes to guess or to fit.

For a pure harmonic crystal, the classical (and quantum mechanical) expression for the dielectric constant at angular frequency ω is[7]

$$\epsilon(\omega) = n_\infty{}^2 + \frac{4\pi e_t^{*2}}{v\mu(\omega_0{}^2 - \omega^2 - i\delta)}. \qquad (1)$$

Here n_∞ is the high-frequency index of refraction; e_t^* is the macroscopic effective charge associated with the $q \approx 0$, TO mode; v the volume of a unit cell; and μ the reduced mass for the two atoms in the unit cell. An infinitesimal amount of damping is provided by $\delta = 0^+$.

With substitutional monovalent impurities we make the change

$$(\omega_0{}^2 - \omega^2 - i\delta)^{-1} \rightarrow (0 \mid \langle G(\omega^2 + i\delta) \rangle \mid 0), \qquad (2)$$

where $G(z) = (A - zI)^{-1}$ is the Green's function matrix for the entire impure crystal; A is the dynamic matrix; $|0)$ is a normalized eigenvector for the $k \approx 0$, TO phonon; and $\langle \cdots \rangle$ denotes a configurational average over impurity sites. G is given in terms of the Green's-function matrix for the perfect crystal:

$$G_0 = (A_0 - zI)^{-1},$$

and the defect matrix Γ, by the expression

$$G = G_0 - G_0\Gamma G_0 + G_0\Gamma G_0\Gamma G_0 - \cdots,$$

which should converge well for weak perturbations Γ.

We assume a "virtual-crystal" model in which the unperturbed phonons diagonalize the mean dynamic matrix

$$A_0 = \langle A \rangle.$$

Then, since $\Gamma \equiv A - A_0$, we have $\langle \Gamma \rangle = 0$, and to lowest order

$$\langle G \rangle = G_0 + G_0 \langle \Gamma G_0 \Gamma \rangle G_0. \tag{3}$$

We shall also need the result

$$G_0(z) \, | 0 \rangle = (\omega_0^2 - z)^{-1} | 0 \rangle. \tag{4}$$

In the experiments described below, only one sublattice, say the positive, carries more than one isotope. Then Γ is a sum of terms over this sublattice of the form

$$\Gamma(L, L') = -\sum_L \Delta M_+(L) \omega^2 \delta(L, L')/M_+,$$

where M_+ is the mean positive-ion mass, $\delta(L, L')$ is the Kronecker δ, and $\Delta M_+(L)$ is the deviation of the true mass at site L from M_+. One can then show that

$$(0 \, | \langle \Gamma G_0 \Gamma \rangle | 0) = (\mu/M_+) G_{++} \langle (\Delta M_+ \omega^2 / M_+)^2 \rangle, \tag{5}$$

where G_{++} is the diagonal matrix element of G_0 at the positive-ion site.

When the expressions (2)-(5) are substituted into Eq. (1) and manipulated, the result for the isotope-induced absorption coefficient becomes

$$\alpha(\omega) = \frac{e_t^{*2}}{ncM_+^3 v} \frac{2\pi^2 \omega^4 \rho^+(\omega)}{(\omega_0^2 - \omega^2)^2} \langle (\Delta M_+)^2 \rangle. \tag{6}$$

Here c is the velocity of light, n the index of refraction at frequency ω, and $\rho_+(\omega)$ is the normalized phonon density of states for the positive sublattice.

We shall follow the suggestion of Szigeti[7,8] and set

$$e_t^* = \tfrac{1}{3} e^* (n_\infty^2 + 2), \tag{7}$$

where e^* is the Szigeti effective charge. Equation (6) with $e_t^* = e^*$ is consistent with results of Maradudin[9] and Benedek and Nardelli[10] in the proper weak-coupling limit. A detailed derivation of the equivalent of (6) and (7) for strong perturbations has been given by Klein.[11]

The absorption measurements were made on single crystals of NaCl and LiF at liquid-helium temperature using a Beckman IR11 spectrophotometer fitted with a beam condenser. The NaCl

crystals were grown in this laboratory from reagent-grade material pretreated for 12 h by bubbling Cl_2 gas through the melt to remove hydroxyl- and carbonate-ion impurities.[6] Analysis of the crystals by a mass spectrograph showed that the major remaining impurity was calcium in concentrations of a few parts per million. Lithium-fluoride crystals containing Li^6 and Li^7 in their natural abundance ratio were supplied by the Harshaw Chemical Company. Isotopically enriched samples were obtained from Pohl at Cornell University. Some were from the same boules investigated by Thacher.[12]

The absorption spectrum at $7°K$ of natural NaCl containing the two stable isotopes of Cl^{35} and Cl^{37} is shown in Fig. 1. Two peaks are observed at 123 and 145.5 cm^{-1} superimposed on the steeply rising Reststrahlen absorption edge. The solid curve is calculated using Eqs. (6) and (7) (with all + subscripts replaced by −'s) with shell-model phonons of Caldwell and Klein.[6] The intensities in the two curves are in very good agreement, particularly considering that the calculated curve involves no adjustable parameters. The two peaks in the theoretical curve are approximately 4% too low. The shape of the absorption is determined largely by the density of states $\rho_-(\omega)$ for the heavier chlorine ion, which is stronger in the acoustic region than in the optical region. We can conclude that the model phonons used have too little energy in the acoustic branches. A recent breathing–shell-model (BSM) calculation by Nüsslein and Schröder[13] gives acoustic-phonon energies up to 5% higher than those from the simple shell model and is more in line with our results.
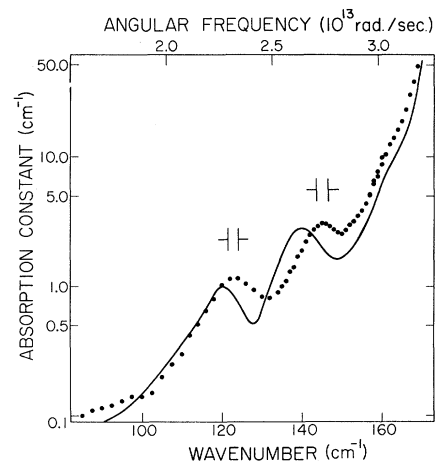

FIG. 1. Band-mode absorption at $7°K$ due to the natural isotopes in NaCl (solid circles, 75.4% Cl^{35}; solid line, calculated curve).

The dispersion curves calculated from both shell models show a complex behavior in the region of the acoustic-phonon critical points which makes assignment of the peaks in our experimental curves to specific Van Hove singularities difficult. The 123-cm^{-1} peak is probably due to transverse-acoustic phonons from the L and W points and from points near the edge of the zone along the Q direction joining them. The 145.5-cm^{-1} peak appears to be associated principally with phonons from the LA(X) critical point.

The LiF data are shown in Fig. 2. Crystals with a mixture of isotopes show a weak peak at 211 ± 2 cm^{-1} together with a stronger one at 252.5 ± 1 cm^{-1}, whereas isotopically pure crystals have only weak, structureless absorption. The relative intensities of the absorption of the isotopically mixed crystals are in the ratio 4.5 :2.9:1, in close agreement with the theoretical ratios of 4.3:3.4:1 predicted by Eq. (6). We conclude that we are indeed observing a true isotope effect rather than an induced absorption from a chemical impurity.

At present we have no detailed shell-model calculation of the absorption for LiF to compare with the experimental data. The BSM density of states and dispersion curves published by Nüsslein and Schröder suggest that our two peaks occur at or close to Van Hove singularities in the transverse-acoustic branches along (111) and (100) directions at TA(L) and TA(X). All other critical points lie either just below or above $k = 0$, TO mode and would be masked by strong Reststrahlen absorption and multiphonon absorption processes. The BSM value for the TA(L) phonon is 204 cm^{-1}; our experimental value is 211 cm^{-1}. The BSM value at the TA(X) point is 238 cm^{-1}; our experiment gives 252.5 cm^{-1}.

Selection rules for defect-induced one-phonon absorption have been derived by Loudon.[14] For an isotopic impurity on the light-ion sublattice of an alkali halide with the NaCl structure, all phonons are infrared active, except for TA and LA at point L and for the singly degenerate acoustical phonon at the point W. For these phonons the light-ion sublattice has zero displacement and thus takes no part in optical absorption. This result appears in conflict with our assignment of the 211-cm^{-1} band in LiF to TA(L). Preliminary shell-model results for LiF show that TA(L) is a saddle point and that there are appreciable numbers of phonons with frequencies close to that of TA(L) for which the light-ion sublattice has nonzero displacements. These pho-
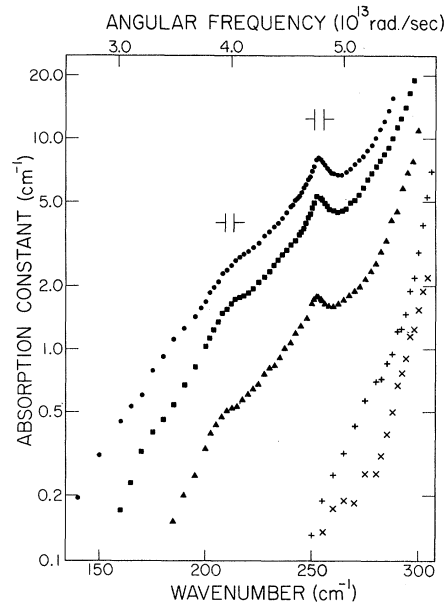

FIG. 2. Band-mode absorption at 7°K due to the lithium isotopes in LiF (solid circles, 50.8% Li^7; solid squares, 69.2% Li^7; solid triangles, 92.6% Li^7 [natural abundance]+ 99.99% Li^7; crosses, 99.99% Li^6).

nons can thus contribute to the weak peak observed at 211 cm^{-1}.

Neutron-determined dispersion curves have recently been obtained for LiF at room temperature by Dolling et al.[15] Their values for the TA(L) and TA(X) points are 207 and 257 cm^{-1}, respectively. These room-temperature values are in close agreement with our low-temperature experimental results and tend to confirm our assignment.

In measurements at 10°K Pierce[16] has observed vibronic peaks displaced from the N bands in LiF by 202 cm^{-1} (and also 210 cm^{-1}) and by 412 cm^{-1}, which he assigned to excitation of one and two TA(X) phonons, respectively. Peaks were also seen at integral multiples of 242 cm^{-1} and identified as TO(L) phonons. These assignments were based on Karo and Hardy's deformation dipole-model calculation for LiF.[17] On the basis of the BSM results mentioned above, we feel that the 202- and 210-cm^{-1} bands are due to phonons near TA(L) and that the 242-cm^{-1} band may be associated with the TA(X) critical point.

An isotope shift in vibronic peaks in LiF has been seen by Hughes.[18] All but one of his peaks lie outside the range of our experiment, the exception being one with a displacement of 212 cm^{-1} in Li^{7}F and 211 cm^{-1} in Li^{6}F. Hughes identified this peak as either TA(X) or TA(L) and

ascribed its weak isotope dependence to the fact that it involved an acoustic mode in which the heavier fluorine ion has most of the displacement. Our spectral resolution was not high enough to reveal isotope shifts. For the 252.5-cm^{-1} band any shift must have been less than 1 cm^{-1}. In the future we plan to look for such shifts with higher resolution. In addition we are currently modifying the shell-model calculation for NaCl to bring it into better agreement with our experimental data. A similar calculation for LiF, including a detailed analysis of the behavior of the optical absorption in the neighborhood of critical points, is also in progress.

The authors would like to thank Professor R. O. Pohl for supplying the isotopically enriched samples of LiF used in this investigation. Thanks also go to Dr. G. Dolling for making available his results on LiF prior to publication.

[1]A. J. Sievers, Phys. Rev. Letters 13, 310 (1964).
[2]A. J. Sievers and S. Takeno, Phys. Rev. 140, A1030 (1965).
[3]R. Weber, Phys. Letters 12, 311 (1964).
[4]R. Weber and P. Nette, Phys. Letters 20, 493 (1966).
[5]H. F. Macdonald and M. V. Klein, in Proceedings of the International Conference on Localized Excitations in Solids, University of California, Irvine, California (to be published).
[6]R. F. Caldwell and M. V. Klein, Phys. Rev. 158, 851 (1967).
[7]E. Burstein, in Proceeding of the International Conference on Lattice Dynamics, Copenhagen, Denmark, 1963, edited by R. F. Wallis (Pergamon Press, Oxford, England, 1965).
[8]B. Szigeti, Trans. Faraday Soc. 45, 155 (1949).
[9]A. A. Maradudin, Astrophysics and the Many Body Problem (W. A. Benjamin, Inc., New York, 1963).
[10]G. Benedek and G. F. Nardelli, Phys. Rev. 155, 1004 (1967).
[11]M. V. Klein, in Physics of Color Centers, edited by W. B. Fowler (Academic Press, Inc., New York, to be published).
[12]P. D. Thacher, Phys. Rev. 156, 975 (1967).
[13]V. Nüsslein and U. Schröder, Phys. Status Solidi 21, 309 (1967).
[14]R. Loudon, Proc. Phys. Soc. (London) 84, 379 (1964).
[15]G. Dolling, H. G. Smith, R. M. Nicklow, P. R. Vijay-araghaven, and M. K. Wilkinson, Bull. Am. Phys. Soc. 12, 557 (1967), and Phys. Rev. 168, 970 (1968).
[16]C. B. Pierce, Phys. Rev. 135, A83 (1964).
[17]A. M. Karo and J. R. Hardy, Phys. Rev. 129, 2024 (1963).
[18]A. E. Hughes, Proc. Phys. Soc. (London) 88, 449 (1966).

THREE-TERM ANALYSIS OF THE IDEAL THERMAL AND ELECTRICAL RESISTIVITIES OF TRANSITION METALS

J. T. Schriempf
U. S. Naval Research Laboratory, Washington, D. C. 20390

Recently there has been considerable interest in the influence of electron-electron interactions on the low-temperature thermal and electrical resistivities of the transition metals. The theoretical treatments[1-3] have typically yielded the resistivities due only to electron-electron scattering; it has generally been assumed (sometimes tacitly) that the effects of other types of scattering can be included by simple addition of the resistivities due to each scattering mechanism. Thus, in analyzing experimental measurements, the following expressions are commonly employed for the low-temperature region:

$$\rho = \rho_0 + AT^2 + BT^5, \tag{1a}$$

$$wT = (wT)_0 + \alpha T^2 + \beta T^3. \tag{1b}$$

Here T is the absolute temperature, ρ the electrical and w the thermal resistivities, respectively; and A, B, α, β, ρ_0, and $(wT)_0$ are the constants. The latter two represent, of course, the behavior of the resistivities in the limit $T \to 0$, where only impurity scattering is effective. Equation (1b) assumes, as is usually the case, that heat transport via the lattice can be neglected. The terms in T^2 are the electron-electron effects, while BT^5 and βT^3 represent the influence of phonon scattering. In order to compare data with the electron-electron theories, the usual practice[2,4,5] is to deduce A and α from the low-temperature slopes of the data on plots of ρ vs T^2 and wT vs T^2. This method avoids the problem of precise determinations of ρ_0 and $(wT)_0$, which dominate ρ and wT at the lower temperatures; on the other hand, it assumes that the phonon terms are negligible.

In a recent Letter[5] we analyzed our simultaneous measurements of the thermal and electri-