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Isotope Effects Induced by Local Modes in the U Band*

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The experimental investigation in the temperature range from 4 to 400°K of the ultraviolet U band in KCl, KBr, and RbCl crystals containing H^- and D^- ions has revealed the following isotope effects: (a) The half-width of the U_H band is from 4 to 8% larger than that of the U_D band. (b) The U_H band occurs at energies $\sim$0.02 eV smaller than those of the U_D band. In order to describe these results the method of moments, in the harmonic and Condon approximations, has been applied. From the symmetry of the defect it is shown that only the vibrational modes which transform according to the Γ_{15}^- representation of the full cubic point group can be responsible for the isotope effects; these modes are just those active in the infrared. It is found that during optical transitions, allowed in dipole approximation, the Γ_{15}^- modes suffer, via the electron-phonon interaction, only a frequency shift, and that only the local mode has to be taken into account in order to predict the observed isotope effects, since the contribution coming from the Γ_{15}^- continuum is negligible. Finally, the local-mode frequency of the excited U center has been estimated.

1. INTRODUCTION

IN recent years considerable attention has been given to the theory of many-phonon processes associated with the absorption or emission of light by impurities in solids.[1–3] Nevertheless a quantitative evaluation of the optical absorption band shape was always performed on the basis of introducing *ad hoc* models, such as the well-known configurational coordinate model.[4] The imperfect-crystal phonon spectrum, indeed, is so complex that accurate calculations can be done either in very simplified schemes, such as the linear chain, or by considering particular phonons, such as the localized ones. Furthermore, the modifications of the phonon field coming from the change of the electron-phonon coupling during the electronic transition increase the difficulty of the computations. In this work we have succeeded in isolating both experimentally and theoretically the effects which are due only to the interaction of the impurity electron with the infrared-active local mode.

Experimentally, the presence of this interaction is shown by different peak energies and half-widths of the absorption bands of H^- and D^- ions (U_H and U_D centers) in alkali halides. A very similar behavior, displayed by the $1s$-$2p$ transitions of H and D atoms diluted in solid Ar, has been reported recently.[5]

Experimental procedures and results are reported in Sec. 2. The theoretical analysis of isotope effects is developed in Sec. 3, where it is shown that isotope effects occur only if the impurities give rise to an infrared-active local mode in the imperfect-lattice dynamics. In the same section, by means of the method of moments, it is shown that the isotope effects depend only upon the interaction of this local mode with the impurity bound electron, both in the ground and in the upper state. This isotope effect does not concern the vibrational continuum, so that it is not necessary to introduce an *ad hoc* model, as one needs to do (Sec. 3c) in the evaluation of the absolute value and the temperature dependence of the band parameters. Finally, the theoretical results and experimental data are compared and discussed in Sec. 4; in the same section an evaluation of the infrared-active mode is made, when the impurity electron is in the excited state.

2. EXPERIMENTAL

KCl and KBr single crystals were supplied as nominally pure by Dr. K. Korth (Kiel, Germany) and RbCl crystals by Semi-Elements, Inc. (Saxonburg, Pennsylvania). The U-centers, i.e., negative hydrogen or deuterium ions in substitutional lattice sites, were produced in the crystals by the following procedure. Firstly, the crystal was additively colored in a Pyrex vial which contained distilled potassium. The crystal was kept in an oven at a temperature of approximately 550°C for 3 h, subsequently cooled to room temperature, and cleaved into plates whose thickness was approximately 1-2 mm. Then colored plates, obtained from the same single crystal, were introduced into a stainless steel container and kept for 20 to 30 min at a temperature of approximately 600°C in the presence of pure H_2 or D_2 gas at a pressure of 2 to 6 kg/cm^2. In order to minimize the concentration of foreign gases, the H_2 or D_2 gas in

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[1] J. J. Markham, Rev. Mod. Phys. 31, 956 (1959).

[2] Y. E. Perlin, Usp. Fiz. Nauk 80, 553 (1963) [English transl.: Soviet Phys.—Usp. 6, 542 (1964)].

[3] See also the references reported in Perlin's review (Ref. 2).

[4] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

[5] G. Baldini, Phys. Rev. 136, 248 (1964).

TABLE I. Experimental results for peak energies and half-widths at $T=6\pm2$°K. The theoretical results are deduced from Eqs. (9) and (10). The units are eV and (eV)^2.

	$\bar{\epsilon}_H$	$\bar{\epsilon}_D$	$\delta\bar{\epsilon}\times10^2$ expt.	$\delta\bar{\epsilon}\times10^2$ theor.	W_H	W_D	$\delta W^2\times10^4$ expt.	$\delta W^2\times10^4$ theory
KCl	5.86±0.005	5.88±0.005	2.0±0.2	2.1	0.25 ±0.005	0.24 ±0.005	49±35	24
KBr	5.51±0.005	5.53±0.005	1.9±0.3	1.7	0.255±0.010	0.235±0.010	98±70	28
RbCl	5.48±0.005	5.50±0.005	2.0±0.2	1.9	0.215±0.005	0.20 ±0.005	63±30	28

the container was renewed a few times during the $F\rightarrow U$ conversion.

Optical measurements were performed using a Tropel grating monochromator equipped with an open Hanovia lamp which was operated with hydrogen at low pressure. The absorption spectra of the *U* centers were obtained by comparing I, the intensity of the light transmitted by the crystals, with I_0, that of the unabsorbed beam, the detector being an EMI 6256-B photomultiplier. The I and I_0 signals were recorded continuously, as a function of wavelength, on a $\frac{1}{4}$-sec-response Brown recorder. The spectral range, 1800 to 2500 Å, was explored at a rate of 100 Å/min with a resolution of ~2 Å, while the lamp output was stable to better than 1% over a time interval of $\frac{1}{2}$ h. The temperature of the crystals, held in thermal contact with the copper block of a metal cryostat, could be varied from ~4 to 400°K and was measured with a AuCo-AgAu thermocouple attached to the crystal.

In Fig. 1 are shown the optical absorption spectra of the U_H and U_D centers in KCl, KBr, and RbCl crystals at liquid-helium temperature. The absorption bands have been normalized to the same height after subtracting the contribution to the absorption coming from the pure crystal in the region of the *U* band; this contribution is assumed to be a linear function of wavelength. The data of Fig. 1 refer to samples with *U*-band optical density at the peak ranging from 1.9 to 3.1 and thickness from 0.2 to 0.7 mm. An estimate of the *U*-center concentration was made by taking for both the U_H and U_D centers the oscillator-strength value evaluated by Martienssen[6] for the U_H center. The concentration was found to be from 2 to 6.5×10^{17} centers per cm^3 for the samples of Fig. 1.

Two isotope effects occurring in the *U* band of the crystals investigated here are easily seen in Fig. 1: (a) the absorption of the U_H centers falls at energies lower than those of the U_D centers, and (b) the half-width of the U_H band is larger than that of the U_D band. In Table I are reported the values of the peak energy and the half-widths of the *U* bands at 6±2°K. Both effects have been studied in the temperature range 4 to 400°K, as illustrated by the following figures. In Fig. 2 the peak energies of the two *U* bands are reported as functions of temperature. The peak position was determined by successively halving the band widths in approaching the band maxima. The band is fairly symmetric, at least for values of the absorption constant larger than 0.3 times the peak value, so that the energy difference between the center of the band measured at one-half of the peak value and the position of the peak is very small ($\lesssim$0.005 eV).

The experimental points of Fig. 2 show that the energy difference between the peaks of the U_D and U_H bands is independent of temperature within the accuracy of the data, and we find for its value 0.020±0.002 eV for the two chlorides and 0.019±0.003 eV for KBr. The larger uncertainty of the KBr data is due to the fact that only three temperatures have been considered for this crystal.

Figure 3 shows the values of the half-widths of the U_H and U_D bands versus temperature in a double logarithmic plot. The half-widths are measured with an uncertainty of ±0.005 eV, with the exception of KBr, which has a larger error because few data were available. As the temperature increases the half-widths of the U_H and U_D bands broaden and become approximately equal within the error on the experimental measures.

As shown in Sec. 3, Eqs. (8) and (9), the peak energies and the half-widths of the *U* bands depend upon the temperature through the angular frequencies ω_1 and ω_2, respectively. The experimental data fitted with the above expression yield the values of ω_1 and ω_2, as shown in Table II. The other parameters appearing in the two equations are derived from the data of Fig. 2 and Fig. 3 and are shown in Table II and Table III. A discussion of the data will be given in Sec. 4.

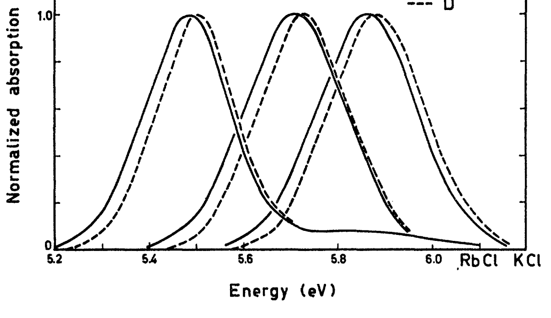

FIG. 1. Normalized optical density spectra of the *U* band of KCl, KBr, and RbCl crystals containing H$^-$ (full line) and D$^-$ (dotted line) ions.

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[6] W. Martienssen, Z. Physik **131**, 488 (1952).

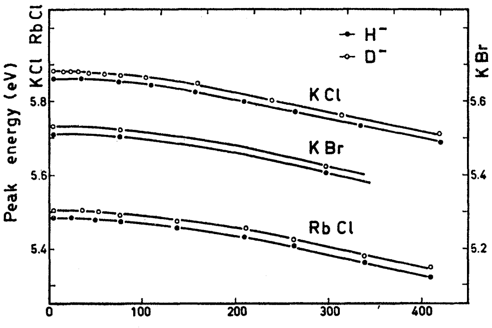

FIG. 2. Peak position versus temperature of the U band in KCl, KBr, and RbCl crystals containing H^- and D^- ions.

3. THEORETICAL

The effects which an isolated impurity in a crystal has on the electron and phonon states can be summarized as follows:

(*i*) *Modification of the electron field.* The imperfection can give rise to localized electron states, usually interpreted as one-electron states of the electron which is more weakly bound to the impurity. This electron, responsible for the optical absorption or emission of the impurity, is often called the "optic" electron. Optic electron states are classified according to the representations of the point group of the symmetry operations which leave the total Hamiltonian invariant. In the case of the U center, the bound levels of the optic electron are classified according to the representation of the O_H point group and fall in the forbidden gap between the valence and the conduction band.

(*ii*) *Modification of the vibrational field.* It is possible to show[4] that a different modification occurs for every optic electron state. In the framework of the adiabatic and harmonic approximations any solution of the normal-mode equation of the imperfect crystal is given[7] by a plane wave plus a diffused wave, if the normal-mode frequency belongs to the vibrational continuum, or by a diffused wave only, if the normal-mode frequency lies outside the continuum, i.e., the normal mode is localized. The amplitude of the localized mode falls off exponentially from the defect, while the amplitude of the diffused wave in the continuum is inversely proportional to the distance from the defect. The diffused wave which appears in all the imperfect normal modes is strongly characterized by the structure of the imperfection itself. It follows that imperfect normal modes are best classified according to the symmetry of the diffused-wave rather than the plane-wave component, when one is interested in the defect properties.

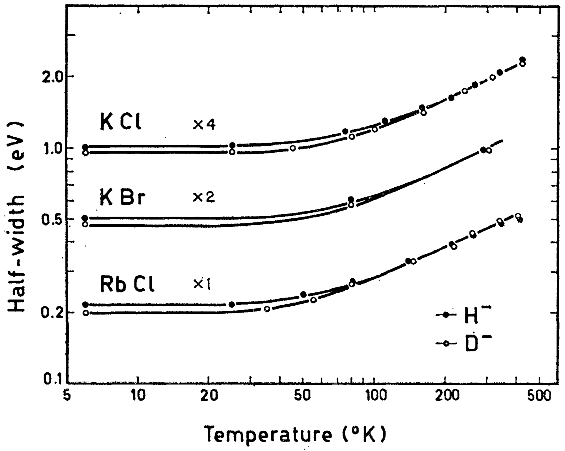

FIG. 3. U band half-width versus temperature for KCl, KBr, and RbCl crystals containing H^- and D^- ions.

In the present work this classification is made according to the irreducible representations of the defect point group. Symmetry operations of the U center are those of the O_H point group (the full cubic point group). Since the O_H point group contains the inversion, the imperfect normal modes can be divided into even and odd modes. By analyzing the perturbation on the dynamical matrix[8] induced by the U center, it turns out that the even Γ_1^+, Γ_{12}^+ and Γ_{15}^+, and the odd Γ_{25}^- and Γ_{15}^- irreducible representations characterize the normal modes. Moreover the Cartesian coordinates of the displacement of the foreign atom are involved in the Γ_{15}^- mode only. Therefore, according to this classification, isotope effects can be accounted for by considering the odd Γ_{15}^- modes corresponding to the two isotopes. These modes are just the infrared-active ones.[9]

A. The Role of the Defect Symmetry in the Many-Phonon Transitions

Following Pekar[10] and Perlin,[2] the quantum states of the optic electron and the states of its coupled vibrational field in the imperfect lattice are defined in the scheme of a suitable adiabatic approximation. This approximation enables us to separate an effective Hamiltonian from the coupled systems even if the electron and the phonons cannot be regarded as weakly interacting systems.

The optic electron, indeed, in several color centers is coupled so strongly with the phonons that many phonons are involved during a transition. In the present approach, the electron-phonon interaction is taken into account in a self-consistent way in both the electron and phonon Hamiltonians. Thus the electron energy

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[7] A. A. Maradudin, in *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin and Company, Inc., New York, 1964).

[8] G. F. Nardelli and N. Terzi, J. Phys. Chem. Solids **25**, 815 (1964).

[9] R. J. Elliott, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1964).

[10] S. I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akademie-Verlag, Berlin, 1954).

levels are functions of the normal coordinates and, vice versa, the "adiabatic" potential in the vibrational Hamiltonian is different for different states of the optic electron. Every electron energy level, when considered as a function of normal coordinates, just represents the adiabatic potential in the corresponding vibrational Hamiltonian. The vibrational Hamiltonians corresponding to two different electron states ν and ν' will be diagonalized by two different systems of normal coordinates $Q_{\nu\lambda}$ and $Q_{\nu'\lambda'}$. It can be shown easily that no system exists which is common to the two electron states. However, it is possible to connect these two systems by a canonical transformation. In the simplest case, when the mixing of the normal coordinates is neglected (i.e., $Q_{\nu'\lambda'}\equiv Q_{\nu'\lambda}$), this transformation can be written as

$$Q_{\nu'\lambda}=-\Delta_{\nu\lambda,\nu'\lambda}+(\omega_{\nu'\lambda}/\omega_{\nu\lambda})^{1/2}Q_{\nu\lambda} \tag{1}$$

if the transition occurs from the ground state ν to an upper state ν'. Here $\omega_{\nu\lambda}$ and $\omega_{\nu'\lambda}$ are the λ normal mode frequencies in the ν and ν' electron states, respectively, and $\Delta_{\nu\lambda,\nu'\lambda}$ is the shift in the value of the λ normal coordinate at which the adiabatic potential (i.e., the electronic level) has its minimum, owing to the change in the electron quantum numbers.

It can be seen from (1) that the two systems of normal coordinates differ for two different reasons.

The first is the displacement $\Delta_{\nu\lambda,\nu'\lambda}$ relative to the λ normal coordinate, here called the "displacement effect." From a static point of view, neglecting anharmonicity effects, this effect arises from the different equilibrium positions that the imperfect lattice ions have when the ν or ν' state is filled by the optic electron. Therefore, $\Delta_{\nu\lambda,\nu'\lambda}$ is a measure of the contribution of every normal mode to the elastic relaxation which occurs after any radiative transition between the ν and ν' states. The displacement of a λ mode belonging to the continuum is proportional to $N^{-1/2}$, N being the number of unit cells in the crystal, while it has a finite value for the local modes.

In Perlin's approach, the displacement effect is due only to the change of the value of H_{int}, the electron-phonon interaction, as evaluated in the ground or in the upper electron states. When only the term linear in the normal modes is retained in the expansion of this interaction, the expectation value of H_{int} in a ν electron state is

$$\begin{aligned}\langle\nu|H_{\text{int}}|\nu\rangle&=\textstyle\sum_\lambda\langle\nu|A_\lambda Q_{\nu\lambda}|\nu\rangle\\&=\textstyle\sum_\lambda\langle\nu|A_\lambda|\nu\rangle Q_{\nu\lambda}\\&=\textstyle\sum_\lambda A_{\nu\lambda}Q_{\nu\lambda}.\end{aligned} \tag{2}$$

So far we have summarized the main qualitative conclusions of Pekar and Perlin's approach. Next we look into the role that the symmetry of both the electron wave function and the normal modes plays in the displacement effect. On analyzing the $A_{\nu\lambda}$ coefficient according to group theory, it follows that $A_{\nu\lambda}$ is different from zero if

$$\Gamma_\nu^2\otimes\Gamma_\lambda\supset\Gamma_1, \tag{3}$$

i.e., if the reduction of the product representation $\Gamma_\nu^2\otimes\Gamma_\lambda$ contains ($\supset$) the identity representation Γ_1. Here Γ_ν, Γ_λ and Γ_1 indicate the representations according to which the ν electron state, the λ normal mode, and the identity transform, respectively. In the case of the O_H group symmetry the condition (3) is satisfied for the U center only when the even λ mode occurs. Therefore, the elastic relaxation which follows a transition from ν to ν' electron states involves even modes only, since for the odd modes

$$A_{\nu\lambda}=A_{\nu'\lambda}\equiv 0. \tag{4}$$

The second reason for a difference between $Q_{\nu\lambda}$ and $Q_{\nu'\lambda}$ consists in the "frequency effect," i.e., the change in frequency from $\omega_{\nu\lambda}$, in the ν electron state, to $\omega_{\nu'\lambda}$ in the ν' state, for any λ normal mode. Indeed, the optic electron wave function is generally more localized around the impurity site when the electron is in the ground state; therefore, soon after the transition and just before the relaxation process takes over, the repulsive forces are weakened, while locally the Coulomb forces can be either strengthened or weakened; however, the over-all effect presumably consists of a weakening of the force constants in the upper electron state when compared with those in the ground state. Rayleigh's theorem[11] states that, under these conditions, every normal-mode frequency in the upper state is smaller than the corresponding one in the ground state. The frequency shift is proportional to N^{-1} for continuum modes, while it is finite, and frequently relevant, for localized modes. Note that the frequency of the local mode may decrease at most to ω_L, the maximum of the vibrational continuum.[11] As we shall see later, it is just this frequency effect which accounts for the isotope effect in the U band.

In conclusion: During the transition the odd modes suffer only the frequency effect, while the even ones suffer both frequency and displacement effect. In other words, in any electron transition allowed in the dipole approximation only even phonons are created or destroyed; therefore, only even phonons participate directly in the many-phonon process, while the odd ones participate indirectly, through the frequency effect. This rule holds also for a more general defect, belonging to the O_H or another symmetry group, when its optic electron undergoes a dipole-allowed transition, insofar as one takes into account the generalization of expression (3). By means of transformation (1) and remembering (3), the difference ΔH between the Hamiltonians H_ν, relative to the electron ground state,

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[11] A. A. Maradudin, E. W. Montroll, and G. M. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963).

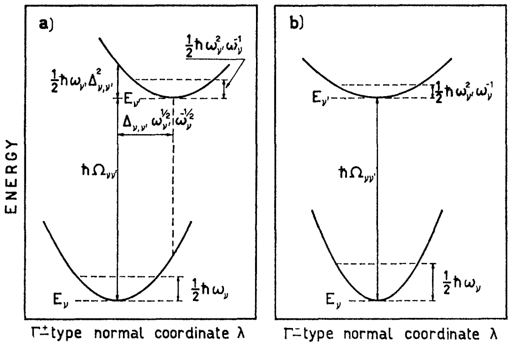

FIG. 4. (a) The adiabatic potential versus an even λ normal coordinate corresponding to the ground electron state (lower parabola) and to the upper state (upper parabola). (b) The adiabatic potentials versus an odd λ normal coordinate corresponding to the ground electron state (lower parabola) and to the upper state (upper parabola).

and $H_{\nu'}$, relative to the upper state, can be written as

$$\begin{aligned}\Delta H/\hbar=&(H_{\nu'}-H_{\nu})/\hbar\\ &=E_{\nu'}/\hbar+\tfrac{1}{2}\sum_{\lambda}\omega_{\nu'\lambda}[Q_{\nu'\lambda}{}^2+(\partial/\partial Q_{\nu'\lambda})^2]\\ &\qquad -E_{\nu}/\hbar-\tfrac{1}{2}\sum_{\lambda}\omega_{\nu\lambda}[Q_{\nu\lambda}{}^2+(\partial/\partial Q_{\nu\lambda})^2]\\ &=\Omega_{\nu\nu'}+\tfrac{1}{2}\sum_{\lambda}^{(+)}\Delta_{\nu\lambda,\nu'\lambda}{}^2\omega_{\nu'\lambda}\\ &\qquad -\sum_{\lambda}^{(+)}\Delta_{\nu\lambda,\nu'\lambda}\sqrt{\frac{\omega_{\nu'\lambda}{}^3}{\omega_{\nu\lambda}}}Q_{\nu\lambda}+\tfrac{1}{2}\sum_{\lambda}^{(+-)}\frac{\omega_{\nu'\lambda}{}^2-\omega_{\nu\lambda}{}^2}{\omega_{\nu\lambda}}Q_{\nu\lambda}{}^2.\end{aligned}\tag{5}$$

$\Omega_{\nu\nu'}=(E_{\nu'}-E_{\nu})/\hbar$ is the frequency of light in a pure electron transition; $\sum_{\lambda}{}^{(+)}\cdots$ and $\sum_{\lambda}{}^{(+-)}\cdots$ indicate that the summations have to be carried out on the even modes only and both the even and odd modes, respectively. Note that the above operator ΔH, when described in the normal coordinate system $Q_{\nu\lambda}$ of the electron ground state, consists of the difference of potential energy only, since in the $Q_{\nu\lambda}$ system the lattice kinetic-energy operators, corresponding to ν and ν' electron states, are the same.

The graphical interpretation of Eq. (5) yields an extension for any λ normal coordinate of the well-known configurational diagram, i.e., the plot of both ν and ν' states versus any single λ normal coordinate; this is possible because one has neglected the mixing of the normal modes. The plots are essentially of two types: one for the even modes, the other for the odd modes [see Figs. 4(a) and (b)]. In the first case the potential-energy minimum for the upper state is shifted with respect to that of the ground state, while in the second plot these minima occur at the same value of the normal coordinate.

B. The Method of Moments

In order to study the properties of the U bands in absorption and to compare theoretical predictions with experimental results, the method of moments[1,2] is employed here. It is well known that by means of this method one can calculate the characteristic parameters such as the mean value, the dispersion, or the asymmetry of a distribution (the absorption band in our case), without knowing directly the distribution law itself (the absorption coefficient in our case). The moments of the absorption band in the Condon approximation are given by the average value of the operator ΔH and its powers with respect to the vibrational states corresponding to the ground electron level. By assuming a nearly Gaussian absorption band, one obtains

$$\bar{\epsilon}(T)=\langle\epsilon(T)\rangle_{\mathrm{av}}=\langle\Delta H\rangle_T \tag{6}$$

for the peak energy $\bar{\epsilon}(T)$ of the absorption band, and

$$\begin{aligned}W^2(T)/8\ln 2=&\langle[\epsilon(T)-\bar{\epsilon}(T)]^2\rangle_{\mathrm{av}}\\ =&\langle\Delta H^2\rangle_T-\langle\Delta H\rangle_T{}^2\end{aligned}\tag{7}$$

for the squared half-width $W^2(T)$. Here $\langle\cdots\rangle_{\mathrm{av}}$ means the average over the band, and $\langle\cdots\rangle_T$ means the average on the vibrational states at thermal equilibrium at temperature T, when the optic electron is in the ground state. Denoting by $\bar{n}_{\lambda}$ the phonon occupation number $[\exp(\hbar\omega_{\nu\lambda}/kT)-1]^{-1}$ for the λ normal mode, and remembering (5), one obtains

$$\begin{aligned}\bar{\epsilon}(T)/\hbar=&\Omega_{\nu\nu'}+\sum_{\lambda}^{(+)}\Delta_{\nu\lambda,\nu'\lambda}{}^2\omega_{\nu'\lambda}\\ &-\tfrac{1}{4}\sum_{\lambda}^{(+-)}[(\omega_{\nu\lambda}{}^2-\omega_{\nu'\lambda}{}^2)/\omega_{\nu\lambda}](2\bar{n}_{\lambda}+1)\\ =&\Omega_{\nu\nu'}+\sum_{\lambda}^{(+)}\Delta_{\nu\lambda,\nu'\lambda}{}^2\omega_{\nu'\lambda}\\ &-\tfrac{1}{4}\sum_{\lambda}^{(+-)}[(\omega_{\nu\lambda}{}^2-\omega_{\nu'\lambda}{}^2)/\omega_{\nu\lambda}]\\ &\qquad\times\coth(\hbar\omega_{\nu\lambda}/2kT);\end{aligned}\tag{6a}$$

$$\begin{aligned}W^2(T)/\hbar^2 8\ln 2=&\tfrac{1}{2}\sum_{\lambda}^{(+)}\Delta_{\nu\lambda,\nu'\lambda}{}^2(\omega_{\nu'\lambda}{}^3/\omega_{\nu\lambda})(2\bar{n}_{\lambda}+1)\\ &+\tfrac{1}{8}\sum_{\lambda}^{(+-)}[(\omega_{\nu\lambda}{}^2-\omega_{\nu'\lambda}{}^2)^2\omega_{\nu\lambda}{}^2](2\bar{n}_{\lambda}+1)^2\\ =&\tfrac{1}{2}\sum_{\lambda}^{(+)}\Delta_{\nu\lambda,\nu'\lambda}{}^2(\omega_{\nu'\lambda}{}^3/\omega_{\nu\lambda})\\ &\qquad\times\coth(\hbar\omega_{\nu\lambda}/2kT)\\ &+\tfrac{1}{8}\sum_{\lambda}^{(+-)}[(\omega_{\nu\lambda}{}^2-\omega_{\nu'\lambda}{}^2)^2/\omega_{\nu\lambda}{}^2]\\ &\qquad\times\coth^2(\hbar\omega_{\nu\lambda}/2kT).\end{aligned}\tag{7a}$$

Let us consider the right member of (6a). The first summation, indicated by $\sum_{\lambda}{}^{(+)}\cdots$, involves only the even modes, which are determined only by the change of force constants and not by the change of mass, the Γ_{15}^- representation being excluded. Moreover, this summation does not depend explicitly on temperature; a very small dependence, here disregarded, could arise from the change of the crystal parameters with temperature.

Both odd and even modes are involved in the second summation of (6a) (indicated by $\sum_\lambda^{(+-)}\cdots$), which accounts for the frequency effect on both continuum and local modes. The temperature variation of the peak energy $\bar{\epsilon}(T)$ is brought about by this second summation via the temperature dependence of $\bar{n}_\lambda$. By means of the experimental results (see Fig. 2), which show that $\bar{\epsilon}(T)$ shifts toward the red when the temperature rises, the sign of the frequency effect is confirmed as predicted earlier, i.e., the λ normal mode frequency $\omega_{\nu'\lambda}$ of the upper electron state is smaller than the corresponding $\omega_{\nu\lambda}$ in the ground state. This temperature shift of $\bar{\epsilon}(T)$ over a wide range of temperatures is accounted for by the continuum modes and by the eventual gap local modes (such as might occur in NaI and KI), because the phonon occupation numbers of these modes depend strongly upon temperature. The local modes well above the continuum are not easily occupied. It is worth noting that this temperature dependence is predicted to be the same for the $U_{\rm H}$ and $U_{\rm D}$ peaks. In fact the contribution coming from the even modes and from the Γ_{25}^- modes is the same for the two centers. Moreover, on the basis of a diatomic linear chain, it is possible to show that the frequencies of the continuum Γ_{15}^- modes differ by a negligible quantity when H^- and D^- are present at small concentrations, and that the frequency effect coming from a possible gap mode is too small to be detected.

Let us consider now the half-width given by Eq. (7a). The second summation is essentially carried out over the localized modes only, since for the continuum modes every term is $O(N^{-2})$. Therefore, the second summation does not change appreciably with temperature, and the thermal dependence of the half-width can be accounted for only by the first summation, which concerns the even modes only.

From the above symmetry considerations it follows that we can separate the contribution to $\bar{\epsilon}(T)$ or $W^2(T)$ due to the even modes of the vibrational continuum from that of all the remaining modes, and specify the terms that give rise to the temperature dependence. However, in order to make a more precise calculation of the coefficients of the N-fold summations appearing in (6a) and (7a), it is necessary to know the interaction law between electron and phonons and to solve the laborious normal-mode equation for the imperfect crystal. This evaluation is beyond the aim of the present work. So, in order to fit the experimental data with an expression containing a finite number of parameters, we have isolated the contribution coming from the Γ_{15}^- local mode and tentatively replaced the other terms in (6a) and (7a) with suitable averaged values, by introducing two effective frequencies ω_1 and ω_2. In other words, these two effective frequencies represent in a concise way all the modes but the Γ_{15}^- local mode, and could be interpreted in the framework of a configurational coordinate model with two frequencies. One obtains

$$\begin{aligned}\bar{\epsilon}(T)=E-B\coth(\hbar\omega_1/2kT)\\ -\tfrac{3}{4}\hbar[(\omega_g^2-\omega_u^2)/\omega_g]\coth(\hbar\omega_g/2kT)\,,\end{aligned}\tag{8}$$

$$\begin{aligned}W^2(T)&=A^2\coth(\hbar\omega_2/2kT)\\ &\quad+3\ln2\;\hbar^2[(\omega_g^2-\omega_u^2)/\omega_g]^2\coth^2(\hbar\omega_g/2kT)\\ &=A^2\coth(\hbar\omega_2/2kT)+C^2.\end{aligned}\tag{9}$$

Here, E stands for the energy of the pure electronic transition plus the mean energy of the even phonons produced during the transition. The energy factor B and the frequency ω_1 have been substituted as effective values in the third term in the right member of (6a), where the sum was performed over all the modes but the Γ_{15}^- local one. Furthermore, A and ω_2 are the effective values introduced in the first term of the right member of Eq. (6a), and ω_g and ω_u are the frequencies, in the ground and in the upper electron state, respectively, of the Γ_{15}^- local mode. We have taken into account the fact that this mode is threefold degenerate. The two frequencies ω_1 and ω_2 are certainly not identical because they represent effective values of two different distributions, averaged on two different sets of normal modes. The expressions (8) and (9) are also better suited than (6a) and (7a) for use in comparing the isotope effects with experimental results, because the contribution of the Γ_{15}^- local mode is isolated in the last terms of the right members.

C. Isotope Effects

The isotope effects occurring in the absorption band of the U center are accounted for in terms of the properties of the infrared-active local mode only. From Eqs. (6a) and (7a), or Eqs. (8) and (9), it turns out that the isotopic shift of the peak energy is given by

$$\begin{aligned}\bar{\epsilon}_{\rm D}(T)-\bar{\epsilon}_{\rm H}(T)&=\delta\bar{\epsilon}(T)\\ &=\hbar\{\tfrac{3}{4}[(\omega_g^2-\omega_u^2)/\omega_g]\coth(\hbar\omega_g/2kT)\}_{\rm H}\\ &\quad-\hbar\{\tfrac{3}{4}[(\omega_g^2-\omega_u^2)/\omega_g]\coth(\hbar\omega_g/2kT)\}_{\rm D}\end{aligned}\tag{10}$$

and the isotopic difference between the squared half-widths is

$$\begin{aligned}W_{\rm H}^2(T)-W_{\rm D}^2(T)&=\delta W^2(T)\\ &=\hbar^2\{3\ln2[(\omega_g^2-\omega_u^2)^2/\omega_g^2]\\ &\qquad\times\coth^2(\hbar\omega_g/2kT)\}_{\rm H}\\ &\quad-\hbar^2\{3\ln2[(\omega_g^2-\omega_u^2)^2/\omega_g^2]\\ &\qquad\times\coth^2(\hbar\omega_g/2kT)\}_{\rm D}.\end{aligned}\tag{11}$$

The symbols $\{\ \}_{\rm H}$ and $\{\ \}_{\rm D}$ mean that the expressions in brackets refer to H^- and D^- isotopes, respectively.

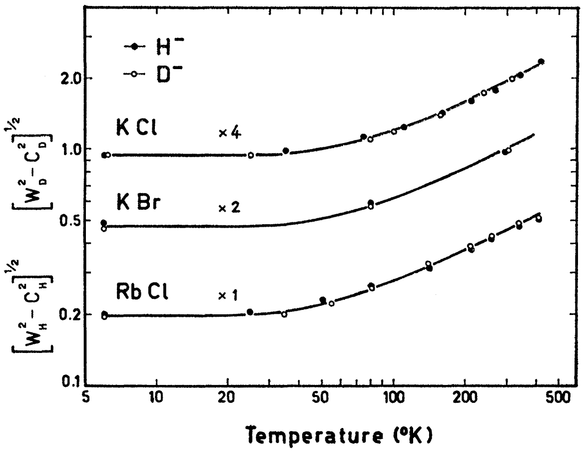

FIG. 5. Half-width of the U_H and U_D bands after subtracting the isotopic contributions C_H^2 and C_D^2 [see Eqs. (9)].

From (10) and (11) it follows that isotope effects are found only if the imperfection gives rise to an infrared-active local mode, and they can be experimentally detected only if the frequency lies well outside the vibrational continuum.

The Γ_{15}^- local-mode frequency for the U_H and U_D centers in the ground state is well known, both from experimental data[12] and from theoretical approaches.[13] It was found that, within a wide range of temperatures and to a good approximation, the relation $(\omega_g)_H = \sqrt{2}(\omega_g)_D$ is verified.[12] In contrast, the Γ_{15}^- local mode in the upper electron state apparently has not been studied. As found earlier, owing to the frequency effect, the local-mode frequencies of the upper state $(\omega_u)_H$ and $(\omega_u)_D$ are smaller than those of the ground state. Therefore, it is also expected[13] that $1 \leq (\omega_u)_H/(\omega_u)_D < \sqrt{2}$ rather than $(\omega_u)_H/(\omega_u)_D = \sqrt{2}$ since for the excited state of the U center at least the nearest neighbors are likely to participate to the Γ_{15}^- local mode.

According to Eqs. (10) and (11), and following the above considerations one can deduce:

(1) $\delta\bar{\epsilon} > 0$: the peak of the U_D band is placed at higher energies than that of the U_H band.

(2) $\delta W^2 > 0$: the U_H band is wider than the U_D band;

(3) the isotope effect is very slightly dependent upon temperature, in the temperature range investigated here, since $\bar{n}_g \simeq 1$ or $\coth(\hbar\omega_g/2kT) \simeq 1$.

TABLE II. Effective constants in eV determined by fitting Eqs. (8) and (9) to the experimental data. ω_u is the local-mode frequency of the upper electron state.

	$\hbar\omega_u \times 10^2$	E	B	$A \times 10^2$	$\hbar\omega_1 \times 10^2$	$\hbar\omega_2 \times 10^2$
KCl	4.1	5.94	0.055	24.2±0.5	1.81	1.24
KBr	2.7	5.57	0.04	24.1±1	1.55	1.12
RbCl	3.3	5.56	0.05	20.3±0.5	1.72	0.93

TABLE III. Infrared active local-mode frequencies for the U_H and U_D centers, in the ground state, at liquid-helium temperature. The last column shows for comparison the maximum theoretical value ω_L of the vibrational continuum. The values of the frequencies are given in eV/$\hbar$.

	$\hbar(\omega_g)_H \times 10^2$	$\hbar(\omega_g)_D \times 10^2$	$\hbar\omega_L \times 10^2$
KCl	6.19[a]	4.45[b]	2.6[c]
KBr	5.51[a]	3.90[b]	2.0[c]
RbCl	5.88[a]	4.16[d]	2.3[c]

[a] G. Schaefer, J. Phys. Chem. Solids 12, 236 (1960).
[b] Values obtained from Ref. 12.
[c] A. M. Karo and J. R. Hardy–see Ref. 14.
[d] Values obtained by putting $(\omega_g)_D = (\omega_g)_H/\sqrt{2}$.

4. CONCLUSIONS

The most interesting feature of the theoretical predictions discussed above is that the isotope effects appear in a straightforward way from the method of moments, in the usual framework of harmonic, adiabatic, and Condon approximations, without introducing an *ad hoc* model. A comparison with experimental data allows us, therefore, to gain some insight, through the value of the local-mode frequency before relaxation, into the dynamical properties of imperfect crystals when the optic electron lies in the bound excited states. Moreover, from the strength and the range of the perturbation on the dynamical matrix, which accounts for the local-mode frequency, some information can be drawn on the adiabatic potential corresponding to the electron in the excited state.

As is shown by Eqs. (8) and (9), the local-mode contribution to the peak position and half-width are related to each other. From the requirement that $\delta\bar{\epsilon}(T)$ and $\delta W^2(T)$ be equal to the corresponding experimental values (see Table I), one can estimate the Γ_{15}^- local-mode frequency for both the U_H and U_D centers in the upper electron state soon after the transition. Unfortunately this evaluation is affected by a large error, because the 5% uncertainty in the measured half-width turns out to give an uncertainty up to 70% in the difference between the squared half-widths. The fitting of the experimental data has been attempted with the two following assumptions: $(\omega_u)_H = (\omega_u)_D$ or $(\omega_u)_H = \sqrt{2}(\omega_u)_D$. The first assumption agrees with the experimental data and the excited-state frequency ω_u is found to fall above ω_L (see Tables II and III). On the other hand, the second assumption does not fit with the data and we are led to the conclusion that both centers have approximately the same behavior in their excited states.

The temperature dependence of the isotope effects, as shown by Eqs. (10) and (11), is negligible, owing to the high energy of the localized modes. This result is in good agreement with the experimental data on both

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isotope effects: The experimental effect on the peak energy is constant and approximately equal to 2×10^{-2} eV; on the other hand, the effect on the half-width at temperatures higher than 100°K probably disappears only in appearance. If we subtract the isotopic contribution, i.e., the last term in the right member of Eqs. (8), from the experimental values of the half-widths W_{H}^2 and W_{D}^2, we obtain the data of Fig. 5; it can be seen that both the points due to the U_{H} and U_{D} centers can be made to fall on the same curve, within the limits of the experimental error.

Finally, we have studied the temperature dependence of the peak energy $\bar{\varepsilon}(T)$ and the half-width $W(T)$. We know the symmetry properties of the continuum modes which give rise to the temperature dependence, but *a priori*, it is difficult to estimate the values of displacement or frequency effects. We have estimated the overall effect by means of two effective frequencies ω_1 and ω_2, which, together with the infrared-active local mode, describe the whole electron-phonon interaction [see Eqs. (8) and (9)]. The values of the two effective frequencies and of the coefficients E, B, and A of Eqs. (8) and (9), determined from the experimental data of Figs. 2 and 3, are reported in Table II. From the frequency distribution reported by Karo[14] for the perfect crystals, one finds that the two frequencies ω_1 and ω_2 fall around the maximum in the transverse optic branch and in the longitudinal acoustic branch, respectively. The considerable difference between ω_1 and ω_2 suggests that a configurational coordinate model with one frequency is not sufficient to describe the optical absorption of the U center or, perhaps, of other centers.

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Role of Longitudinal and Transverse Phonons in Lattice Thermal Conductivity of GaAs and InSb

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The lattice thermal conductivity of GaAs and InSb has been calculated in the temperature range 2–300°K taking into consideration the details of phonon dispersion relations resulting in the separate contributions of the longitudinal and transverse phonons. This analysis gives a much better fit to the experimental data throughout the whole range of temperature than is given by Callaway's formulation which is based on Debye's phonon spectrum, a choice of relaxation time for phonon-phonon scattering relaxation time which is valid for longitudinal phonons, and the use of the average phonon velocity.

1. INTRODUCTION

THE problem of lattice thermal conductivity of substances in which heat is primarily carried by phonons, has been thoroughly investigated in recent years.[1–10] An exact treatment of the problem, however, is hampered by the lack of knowledge of the crystal vibration spectra and the anharmonic forces, and by the difficulty of obtaining exact solutions of the Boltzmann equation. A much-simplified model was proposed by Callaway assuming a Debye phonon spectrum consisting of one average (acoustic) branch and making several assumptions as to the form of the three-phonon-scattering relaxation times. This model has been successfully applied to a number of substances.[11–14]

Holland[15] has studied lattice thermal conductivity of GaAs and InSb in the temperature range 1.7° to 300°K and compared the experimental results with the analysis based on Callaway's model which could not explain the entire temperature dependence of thermal conductivity. There is a change in the slope in the experimental data at about 80°K in InSb and about

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