PHYSICAL REVIEW VOLUME 185, NUMBER 3 15 SEPTEMBER 1969

Microwave Sound Absorption by Anharmonic Three-Phonon Interactions in TiO_2

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(Received 17 March 1969)

Hypersonic attenuation has been measured, for both polarizations, along the *c* axis of rutile single crystals in the frequency range from 0.5 to 3 GHz and at temperatures from 4 to 60°K. For shear waves, the attenuation varies roughly as ΩT^4. For longitudinal waves, the attenuation gradually departs from this behavior towards a lower frequency dependence and a higher temperature dependence as the crystal temperature is reduced. For both types of waves, the frequency and temperature dependence of the absorption coefficient is in good agreement with those theories that include finite thermal-phonon lifetime and acoustic dispersion effects in the absorption of hypersonic waves by anharmonic interactions with thermal phonons.

INTRODUCTION

THE role of anharmonic interactions in the absorption of high-frequency acoustic waves in perfect dielectric crystals is well established both theoretically[1–6] and from a growing number of experiments.[7–16] At high temperatures where $\Omega\tau < 1$, Ω being the sound wave frequency and τ the phonon relaxation time, the dominant absorption mechanism is the one originally proposed by Akhiezer,[17] which later was successfully applied by Mason and by others[18–21] to measurements on a number of insulating crystals. The ultrasonic wave modulates the frequencies of the thermal phonons, which subsequently relax toward local equilibrium by anharmonic phonon-phonon collisions at the expense of wave energy. The phonon relaxation time involved in the high-temperature absorption is experimentally of the same order of magnitude as the thermal conductivity relaxation time.

Simons[22] has recently shown that a Boltzman equation treatment of hypersonic absorption at low temperature ($\Omega\tau > 1$) is valid for arbitrary thermal-phonon mean free paths as long as $\hbar\Omega < kT$. However, the low-temperature absorption problem has usually been treated microscopically by considering the external wave on similar bases as the thermal phonons with which it interacts by three-phonon N processes. Landau and Rumer[1] first used this approach and found that only transverse waves of low energy could be absorbed by anharmonic interactions with thermal phonons. Orbach[2] comprehensively extended their work to include Umklapp and fourth-order collisions and found them to be unimportant absorption mechanisms in the low-temperature range. Experimentally it is observed that the absorption of transverse waves for many solids varies like ΩT^4 as predicted by Landau and Rumer, even though low symmetry crystals show a departure from that relation at the lowest temperatures. Longitudinal waves show an absorption whose magnitude is not too different from that of transverse waves. It follows, over a certain range, an ΩT^4 law, but recently a higher-temperature and lower-frequency dependence has been observed when the temperature is lowered sufficiently.

The attenuation of longitudinal waves and the departure in the attenuation of transverse waves from the ΩT^4 law have been attributed to finite thermal-phonon lifetime and acoustic dispersion effects. If τ is finite, the selection rules for three-phonon processes are relaxed to include collinear and other forbidden collisions which now contribute to the absorption. As the anharmonic interaction process is most effective for those phonons that can keep up with the ultrasonic wave,[9] it is to be expected that collinear processes will be limited by acoustic dispersion and that at some low temperature they may become ineffective (as pointed out in Ref. 11). Since there may be two or more different

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phonon processes active in the absorption of a given ultrasonic wave, the predominant process being determined by the size of the relevant parameters, one should expect that a wave of a given polarization would show an absorption with different temperature and frequency dependence when measured in different materials.[23] It has been observed experimentally in a number of cases[9,13–16] that longitudinal wave absorption changes from an ΩT^4 dependence to a T^7 or T^9 dependence as the temperature is decreased. It should be pointed out that the above mentioned dependences are theoretically obtained as limiting cases by assuming that the thermal-phonon relaxation time τ is either infinite or is the N-process relaxation time with a T^{-5} temperature dependence. This latter assumption will not be valid for materials which show a strongly temperature-dependent attenuation at temperatures around or above the temperature corresponding to the maximum of the thermal conductivity.[24]

Since the absorption of hypersonic waves in perfect insulating crystals at low temperatures is mainly determined by their anharmonic interaction with thermal phonons, acoustic attenuation measurements are potential sources of information about the strength of such interactions in solids over a wide frequency and temperature range. Of particular interest is the N-process phonon relaxation time which enters directly in the formulation of the theories of acoustic absorption at the lowest temperatures and about which few other measurements can give direct information. It is the purpose of the present study to make a careful comparison between attenuation experiments and a theory that includes a measure of elastic anisotropy. Rutile has been chosen for the present work since it is one of the materials with lowest acoustic losses in the microwave range. Also its thermal properties have been studied over a wide temperature range by several authors.[25–27]

EXPERIMENTAL METHODS AND RESULTS

The measurements were performed using conventional ultrasonic pulse-echo techniques. Pulse microwave signals of a few hundred watts peak power, 1-μsec duration, and a repetition rate of about 200 per sec were critically coupled into tunable reentrant cavities. Attached to one surface of the rutile specimen to be measured there was a piezoelectric transducer, and this surface was exposed to the rf field of the cavity for the generation of hypersonic pulses. The same cavity was used as a detector for the multiple acoustic reflections in the sample. The resulting echo pattern amplified in a superheterodyne receiving system was displayed on the oscilloscope and photographed. The receiving system was protected during the transmitter pulse by coaxial magic tees.

Specimens used were of 4-mm-square cross section, 25-mm-long prisms with end surfaces optically flat to $\frac{1}{10}$ wavelength of sodium light and parallel to 4 sec of arc. Side surfaces were fine ground. Rod axis is aligned to within 20 min of arc of the crystallographic c axis.[28] Transducers were either thin resonant quartz disks driven at high harmonic and bonded to the specimen by 200-centistoke viscosity silicon oil or thin CdS films deposited under high vacuum directly onto the end surfaces of the samples.[29]

The cavity with the specimen could be cooled to 1.5°K. During measurements the cavity and specimen were placed in helium gas at atmospheric pressure. The temperature was determined by means of thermocouples (gold+2.1-at.% cobalt versus copper) placed next to the sample and calibrated against a gas thermometer.

The attenuation was determined by measurements of the height of the echo pulses. For the measurements of very small attenuations at the lower temperatures pulses were used which were separated by 50 round trips in the 25-mm-long samples. The absorption relative to 4°K was independent of the type of transducer used, but measurements with CdS transducers showed smaller residual attenuation at helium temperature. In general the residual attenuation was greater for transverse waves than for longitudinal waves.

The measured absorption in dB/cm, corresponding to hypersonic waves propagating along the c axis of rutile crystals is plotted in Figs. 1 and 2 (1 Np$=$8.68 dB). The temperature-independent residual absorption has been subtracted. Longitudinal waves show an ΩT^4 absorption followed by a lower frequency and a greater temperature dependence at the lower range. Transverse waves display the ΩT^4 Landau-Rumer behavior down to the lowest temperature.

In making comparisons with theory the measured thermal conductivity will be taken from the paper of Thurber and Mante[27] as well as a formula for the thermal-phonon relaxation time τ, which gives the best agreement with the measurements reported there. This formula neglects the effects of phonon-phonon normal processes in τ. Figure 3 shows the curve of τ versus temperature calculated for different values of the reduced dominant thermal-phonon frequency n. For a frequency of 1 GHz, $\Omega\tau=1$ at around 40°K. The density of rutile is taken as 4.26 g/cc [20] and the Debye temperature T_D for the longitudinal mode as calculated from the room-temperature lattice constant ($a=2.96$ au) by the relation $T_D=\hbar v_L/2ka$, is 887°K. Longitudinal and transverse wave velocities along the c axis are taken as 10.9 and 5.4 km/sec, respectively.[30]

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THEORETICAL INTERPRETATION

It has been shown elsewhere[31] that for $\hbar\Omega < kT$ and $\Omega\tau > 1$, a Boltzmann-equation treatment of the problem has the advantage of including systematically the elastic anisotropy in the Debye anisotropic model by the use of generalized Grüneisen parameters. When such an approach is utilized one obtains for the low-temperature absorption coefficient (in Np/cm)

$$\alpha_j = \frac{\hbar\Omega}{(2\pi)^3\rho c_j^3}\sum_i \int_0^{\omega_{\max}{}^i} d\omega_i \int_0^{\pi} d\theta_i \int_0^{2\pi} d\varphi_i \times \frac{\omega_i^4}{v_i^3}\frac{\partial f_i}{\partial\omega_i}\gamma_{ij}^2\frac{\Omega\tau_i\sin\theta_i}{1+(\Delta_i\tau_i)^2}, \qquad (1)$$

where j refers to the polarization of the sound wave of frequency Ω and velocity c_j; i refers to the thermal mode which is perturbed by the wave; f_i is the unperturbed equilibrium distribution of the thermal mode of unperturbed frequency ω_i, group velocity v_i, and relaxation time τ_i; γ_{ij} denotes the appropriate component of the generalized Grüneisen parameter as defined by Brugger[32]; θ_i and φ_i are the angles which the thermal-phonon wave vector makes with the wave propagation direction, the latter being considered as the polar axis; ρ is the density of the solid; and $\Delta_i = \Omega(1 - v_i\cos\theta_i/c_j)$ (in the interaction picture Δ_i would correspond to the energy deficit between initial and final phonon states). By keeping our formulation in terms of the phonon group velocity, we retain the possibility of examining

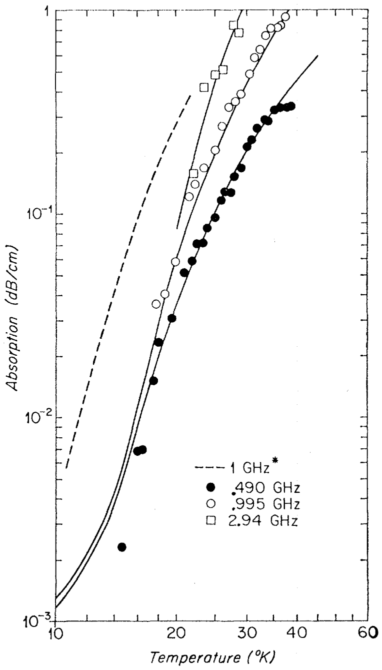

FIG. 1. Temperature-dependent attenuation coefficient for longitudinal waves propagating along the c axis in rutile. Dashed curve gives Lange's results (Ref. 30); solid curve indicates theory.

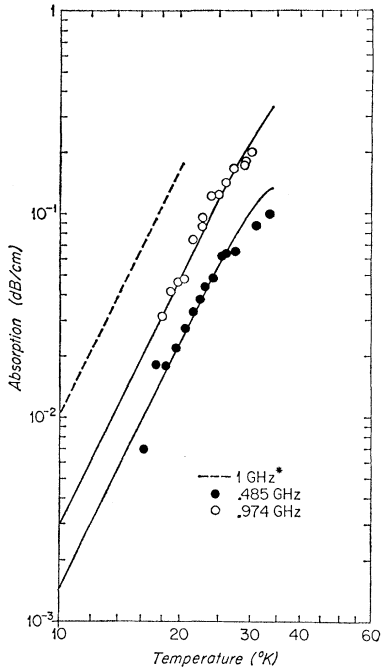

FIG. 2. Temperature-dependent attenuation coefficient for transverse waves propagating along the c axis in rutile. Dashed curve gives Lange's results (Ref. 30); solid curve indicates theory.

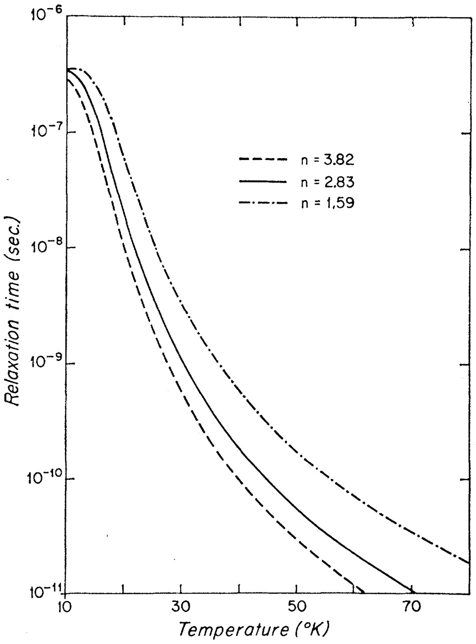

FIG. 3. Thermal conductivity relaxation time for rutile crystals for different values of the dominant thermal-phonon reduced frequency $n = \hbar\omega/kT$.

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the effect of acoustic dispersion on the absorption coefficient for collinear phonon processes. We will take dispersion into account for such cases assuming a linear chain model for the thermal mode involved and keeping only quadratic terms in the thermal-phonon frequency or wave vector.

In order to simplify Eq. (1), the following assumptions will be made: (a) Each mode i is assumed to have isotropic properties in the sense that v_i and τ_i are taken to depend only on the magnitude of phonon wave vector $\mathbf{q}$, but the direction of particle displacement in the mode and its direction of propagation are considered to remain either collinear or orthogonal. Hence each mode i is taken as a pure longitudinal or pure transverse mode of the crystal with the same functional form for γ_{ij} throughout q space. (b) Since $\omega_i^4 \partial f_i/\partial\omega_i$ is maximum at $\hbar\omega_i = 3.8kT$, while the rest of the integrand is a relatively slowly varying function of ω_i, we replace τ_i and $1-v_i/c_j$ by the values they will have at $\hbar\omega_i = nkT$, where n is taken as an adjustable parameter of order 1. With the above assumptions we arrive at

$$\alpha_j = \frac{\Omega k^4 T^4}{\rho v_i^4 c_j^2 \hbar^3} \sum_i J_4\!\left(\frac{T_{Di}}{T}\right) \int_0^\pi d\theta_i \times \frac{\Omega\tau_i \sin\theta_i}{1+(\Delta_i\tau_i)^2} \int_0^{2\pi} \gamma_{ij}^2(\theta_i,\varphi_i)\,d\varphi_i, \quad (2)$$

where J_4 is the transport integral which arises in the Debye formula for the specific heat of a solid, and the summation is taken over the thermal modes which are allowed to interact with a given wave. There exist in the recent literature[18,19,21] extensive tables of γ_{ij} for waves propagating along the $\langle 100\rangle$ and $\langle 111\rangle$ axes of cubic crystals.

To determine the component of the Grüneisen parameter which should enter into Eq. (2), one has first to establish the allowed interaction processes for a given acoustic wave propagating along the c axis of a crystal of class D_{4h}. For the usual experimental case where the wave frequency is much smaller than the dominant thermal phonon frequency, the most probable process is that in which the wave interacts with a thermal phonon and creates another thermal phonon of the same mode.[2] Applying considerations of energy and wave vector conservation (appropriately relaxed by the uncertainties in these quantities), one arrives at the condition that an allowed interaction process is most effective for a phonon with wave vector along those polar angles that satisfy the relation

$$(c_j/v_i)(1-1/\Omega\tau_i) \le \cos\theta_i \le (c_j/v_i)(1+1/\Omega\tau_i).$$

Thus, the interaction is most effective over a narrow sector of solid angle around $\theta_i = \arccos(c_j/v_i)$. The result also implies that $v_i \ge c_j(1-1/\Omega\tau_i)$, which is equivalent to our previous statement that the effectiveness of a given process in the absorption of a sound wave is maximum for those phonons that can keep up with the wave for a substantial number of wavelengths. The above conditions require that among all possible interaction processes only the following types be considered[33] (1 denotes the microwave phonon, 2 and 3 label the thermal phonons, L and T indicate polarization):

(a) $T_1 + L_2 = L_3$,
(b) $T_1 + T_2 = T_3$,
(c) $L_1 + T_2 = T_3$,
(d) $L_1 + L_2 = L_3$.

Process (a) was first considered by Landau and Rumer as responsible for the absorption of transverse waves in solids. It can be shown that in this case dispersion effects do not appreciably change the results and thus can be safely neglected. The Grüneisen parameter for this process, already averaged over azimuthal angle is

$$\langle\gamma_a^2\rangle = \tfrac{1}{4}\pi[(C_1\cos^4\theta + C_2\cos^2\theta + C_3)/2C]^2,$$

where $C_1 = 4C_{166} - 2C_{366} - 2C_{456}$, $C_2 = 2C_{456} + 2C_{366} - 8C_{166} - 2C_{66} - 2C$, and $C_3 = 4C_{166} + 2C_{66} + 2C$. C is the effectime second-order elastic modulus that determines v_L along the direction $\theta = \arccos(c_T/v_L)$. We do not include here the contribution from another process of type (a): $T_1 + T_2' = T_3'$, where T' represents a thermal phonon with $v_T > c_T$. Since its contribution to the absorption coefficient for $\Omega\tau \gg 1$ will differ from that of process (a) only in the size of an effective coupling constant $(\gamma/v_T^2)^2$.

For process (b) the resulting γ is much smaller than for process (a). In general it is true that transverse waves propagating along a twofold axis do not couple with collinear transverse phonons. Process (c) has been considered in the literature[23] as responsible for the absorption of longitudinal waves in some materials that show a T^9 dependence in the absorption coefficient at the lowest temperatures. From the condition on the ratio v_i/c_j we deduce that it would be important for waves propagating along crystal axes not to have different longitudinal and transverse wave velocities. As this is not the case for propagation along the c axis in rutile we need not consider this process any further.

The case (d) corresponds to the so-called collinear or quasicollinear process, one which has been invoked to explain the absorption of longitudinal waves in various crystals.[9,11,34,35] As already pointed out, the effectiveness of this process is determined by the competition between finite lifetime and dispersion effects. The corresponding Grüneisen parameter, av-

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[33] We do not consider here the mechanism of absorption proposed by C. Herring [Phys. Rev. **95**, 954 (1954)], since the corresponding absorption coefficient is too small and its temperature and frequency dependence also conflicts with experiments.

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eraged over azimuthal angle, is

$$\langle\gamma_d^2\rangle = 2\pi[(3C_{33}\cos^2\theta + C_{333}\cos^4\theta)/2C_{33}]^2.$$

Since for collinear processes the angle θ is extremely small, we have neglected the terms in $\sin\theta$ to arrive at the preceding expression.

Substituting the above calculated values of the Grüneisen parameters into Eq. (2), we obtain the following approximate formulas for the low-temperature absorption coefficient of transverse and longitudinal waves, respectively (in Np/cm):

$$\alpha_T = \frac{\pi\Omega k^4T^4J_4}{4\rho v^4 c_T{}^2\hbar^3}\left[\frac{C_1(c_T/v)^4 + C_2(c_T/v)^2 + C_3}{2C}\right]^2 \times\left(\pi - \frac{1}{\Omega\tau}\,\frac{2v/c_T}{(v/c_T)^2-1}\right), \quad (3)$$

$$\alpha_L = \frac{2\pi\Omega k^4T^4J_4}{\rho v^4 c_L{}^2\hbar^3}\left[\frac{3C_{33}(c_L/v)^2 + C_{333}(c_L/v)^4}{2C_{33}}\right]^2 \times\arctan\frac{2(v/c_L)\Omega\tau}{1+[1-(v/c_L)^2]\Omega^2\tau^2}. \quad (4)$$

In Eq. (3), $C=\rho v^2$ and c_T is the velocity of transverse waves along the c axis. In Eq. (4), c_L is the velocity of longitudinal waves along the same axis, here v/c_L may be taken as 1, except in the denominator of the argument of arc tangent, where it should be replaced by $1-\frac{1}{2}\times(nT/2T_D)^2$ to take proper account of acoustic dispersion. In this approximation, Eqs. (3) and (4) will give ΩT^4 and T^7, respectively, for the temperature and frequency dependence of the absorption coefficient at the lowest temperature, if τ is taken proportional to T^{-5}. The same results could have been obtained if instead of performing the complete θ integrations one were to replace $\langle\gamma_{ij}{}^2\rangle_\varphi$ by its value at $\theta_i = \arccos(c_j/v_i)$ and integrate only the Breit-Wigner function in Eq. (2). This procedure would permit one to include in a simple way anisotropy effects in the calculation of the absorption coefficient for crystals. In what follows we will refer to the bracketed terms in Eqs. (3) and (4) as $\gamma_T{}^2$ and $\gamma_L{}^2$, respectively.

COMPARISON WITH EXPERIMENTS

The results of the calculations for the absorption coefficients by means of formulas (3) and (4), are represented by the solid-line curves of Fig. 1 and 2. For both polarizations the best fits were obtained with a reduced thermal-phonon frequency, $n=2.8$. This value maximizes the function $n^3/(e^n-1)$. For longitudinal waves the fittings were done for the 490-MHz data at a temperature of 26°K. This gives for $[(3C_{33}+C_{333})/2C_{33}]^2$ a value of 241. Using the published value[36] for C_{33}, the anharmonic constant $3C_{33}+C_{333} = \pm 140\times 10^{12}$ dyn/cm². For transverse waves, the theory was fitted at 18°K for the 974-MHz experiments. Since $\Omega\tau \gg 1$, the true value of v/c_T has little effect on the final result, and we have taken it to be 1.85. For this case the coupling constant $\gamma_T{}^2 = 87.6$. (To the authors' knowledge no measurements of the third-order elastic constants of rutile have been published.) For both polarizations the observed frequency and temperature dependence of the absorption coefficient is well described by the theory in spite of the gross approximations made. As can be seen from the graphs, the theory does not work well at the lowest-temperature range for longitudinal waves. This is most probably due to the fact that the τ used in calculations does not take into account N processes which effectively reduce the low-temperature phonon lifetime that enters into Eqs. (3) and (4). If these extra scattering mechanisms are taken into account, the resulting τ will increase faster at low temperatures (Fig. 3), and it will reduce the calculated absorption coefficient.

There exist large discrepancies between our experiments and previous measurements of hypersonic absorption in rutile,[30] the difference being too large to be attributed to experimental uncertainties. It is possible that previous experiments have been done on imperfect crystals and do not show the true absorption of the material. One of the reasons that lead us to believe that our data are more representative of the intrinsic absorption in rutile is that at 20°K the measured absorption coefficient for 500-MHz longitudinal waves is about half the value of that in Z-cut quartz crystals.[9] It was evident experimentally that the absorption in rutile is smaller than in quartz, since the observed echo trains for a given frequency, both at low and high temperatures, were considerably larger for rutile in crystals of comparable lengths. Using in Eq. (3) the published values of the parameters for quartz,[37,38] we find that for longitudinal waves propagating along the c axis, the ratio of absorption coefficients is around 1.8 (at 500 MHz and 20°K), in good agreement with experiment. Sample dependent acoustic attenuation in rutile crystals has been reported.[39]

CONCLUSIONS

We have measured the hypersonic attenuation of longitudinal and transverse waves along the c axis of rutile single crystals at low temperatures. The temperature and frequency dependence of the absorption is interpreted as due to anharmonic interactions of the wave with thermal phonons. Over most of the tempera-

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[38] H. J. McSkimin, P. Andreatch, and R. N. Thurston, J. Appl. Phys. **36**, 1624 (1965).

[39] T. A. Midford and S. Wanuga, J. Appl. Phys. **36**, 3362 (1965).

ture range good agreement is obtained for both polarizations from calculations that include lifetime and dispersion effects in the anisotropic Debye model. In the calculations it appears valid to use the thermal-phonon lifetime as obtained from thermal conductivity measurements except at the lowest temperatures, where the effect of N processes on the phonon relaxation time becomes important for acoustic absorption. From the coupling constants resulting from the fitting of the theory to the experimental data it is possible to obtain the magnitude of the anharmonic constant $3C_{33}+C_{333}$ for the material. Large discrepancies are found with previous attenuation measurements which may be attributed to imperfect rutile samples.

ACKNOWLEDGMENTS

The authors wish to thank Miss R. Oentrich for her technical assistance in the preparation of the film transducers. We are most grateful to James N. Lange for communicating his results to us prior to publication.

PHYSICAL REVIEW VOLUME 185, NUMBER 3 15 SEPTEMBER 1969

Regularities between Exciton States and F-Center Excited States of Alkali Halides

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(Received 17 February 1969)

The extent to which the intrinsic and the F-center absorption for alkali halides have common features has been explored by plotting the respective band photon energies against each other. Of the many possible binary combinations of excitonic and F-center energy-level separations for the nine potassium, rubidium, and cesium chlorides, bromides, and iodides, two sets of corresponding bands can be recognized for each halide by the very nearly equal energy separations between the exciton fundamental and the F band, i.e., $\Delta h\nu(\text{intrinsic})=\Delta h\nu(F\text{ center})$. The remaining structure in the excitonic spectra can then be attributed to upper components of halogen doublets. Splittings are very nearly constant for the iodides. The first two bands of the modified Rydberg exciton series, which converges at the conduction-band edge, correlate with the F and K bands. The L bands comprise another series which, with their corresponding excitonic bands, exhibit a linear dependence on the consecutive energy levels of the free alkali atom.

I. INTRODUCTION

THE intrinsic absorptions at $\sim$80°K of $\sim$100-Å alkali halide films reported by Eby, Teegarden, and Dutton[1] (ETD) and at 10°K reported by Teegarden and Baldini[2] (TB) exhibit in each instance a strong band with multiplet structure at onset in the far ultraviolet, followed usually by a step, then by other more or less pronounced structure. Fischer and Hilsch[3] used $\sim$1000-Å films of the alkali halides at $\sim$10°K to establish structure in the step region (since confirmed[2]). This they attributed to the $n=2$ level in the hydrogenic, effective-mass model of the exciton, the band at onset corresponding to $n=1$. The sharp, intense character of this band has been attributed[4] to the single-particle function which describes the electron principally involved in the transition as localized. Reflectivity measurements for single crystals at 55°K by Baldini and Bosacchi[5] have resolved new detail for the excitonic transitions. These authors have compared the energy differences between the K and L_1 bands with those between X_3 and Γ_1 excitons for K and Rb halides, finding fairly close agreement. They also suggested a possible relationship between the L_2 and L_3 peaks and the conduction bands. A detailed comparison of F, K, and L bands (hereafter FKL) with intrinsic absorption spectra is presented here; it provides strong, though purely empirical, evidence of correspondence between bands in the two spectra for several alkali halides.

II. COMPARISON OF SPECTRA

To facilitate the search for possible similarities between exciton band energies $h\nu_e$ and FKL band energies $h\nu_F$, these quantities have been plotted against each other in Figs. 1(a)–1(i). The data for excitonic transitions have been taken from the work cited,[1,2,5] and Moran's[6] triplet resolution of the exciton fundamental for Cs halides is also included. The data for F-center

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* The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-658.

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