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Infrared Dielectric Properties of Cadmium Fluoride and Lead Fluoride*

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Infrared reflectivity measurements have been made on samples of cubic CdF_2 and PbF_2 between 10 and 150 μ at room temperature. The data have been analyzed by the use of reflectivity dispersion relations to obtain infrared dielectric properties of these substances as well as their optic-mode frequencies (transverse and longitudinal, TO and LO). For CdF_2 we find $\omega_{TO}=202$ cm^{-1}; $\omega_{LO}=384$ cm^{-1}; $\epsilon_s=8.09$. For PbF_2, $\omega_{TO}=102$ cm^{-1}; $\omega_{LO}=337$ cm^{-1}; $\epsilon_s=27.4$.

I. INTRODUCTION

CADMIUM fluoride and lead fluoride are optically transparent insulators which crystallize in the fluorite structure.[1] Perhaps the most noteworthy property of CdF_2 yet to come to light is the discovery of a series of electron donors that convert CdF_2 into a high-band-gap (6.0 eV) n-type semiconductor.[2] It also accepts trivalent rare-earth ions readily and has been investigated as a fluorescent host.[3] There is some interest in PbF_2 as an optical material because of its high dispersion in the visible region.[4,5] In determining the dielectric response of these lattices we were motivated partly by the possible utility of such data in the understanding of the electrical transport properties of CdF_2 in terms of polaron theory.

II. EXPERIMENTAL METHODS AND RESULTS

Starting material for the PbF_2 crystal growth was obtained from British drug houses, "Reagent Grade." The material was regrown in a two-zone modified Stockbarger furnace with a flowing (2 liter/min) argon atmosphere. The thin-walled $\frac{5}{8}$-in.-diam graphite crucible was lowered at a rate of $\sim 1\frac{1}{8}$ mm/h. The top zone was controlled at 900°C, the lower at 750°C. (The approximate melting point is 825°C.) Several such crystallizations, retaining only the best portion at each stage, finally resulted in an optically homogeneous, (probably) single crystal two inches in length. The single-crystal samples of CdF_2 used were purchased from Optovac Corporation.

Samples of both materials were cut and polished by using standard metallographic procedures, the final polish being 0.05 μ alumina. After the reflectivity of the polished surfaces was measured, the surfaces were acid etched and the reflectivity rechecked. No systematic differences were detected between the two methods of preparation. The reflectivity was measured by a point by point comparison with an aluminized surface in a Perkin-Elmer model 301 spectrometer. The measurements were corrected for the reflectivity of the aluminum but not for the off-axis configuration (9° angle of incidence). The spectral slit widths used varied from 1 to 6 cm^{-1}. No systematic check for scattered light was performed, but the reflectivity of CaF_2 was determined as a control and agreed with the published measurements of Kaiser *et al.*[6] to within $\sim 2\%$ over the entire range. The results are shown in Figs. 1 and 2. The low-frequency dielectric constants were determined by measuring the capacitance of several-mm-thick disks of sample material in a conventional Schering bridge circuit.

The refractive index n and extinction coefficient k of these materials can be specified in terms of a complex reflectivity

$$\rho=\left(\frac{n-ik-1}{n-ik+1}\right)=R^{1/2}e^{i\theta}. \qquad (1)$$

Although the phase shift θ of the reflected electric field with respect to the incident field is lost in the

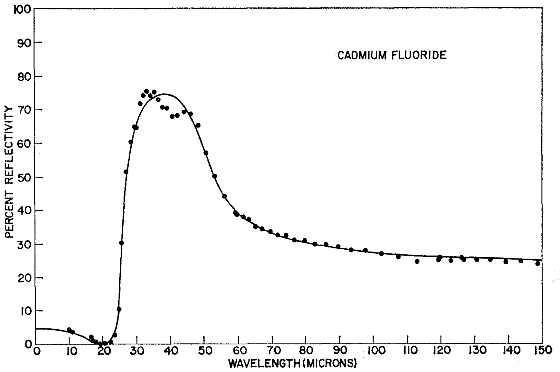

FIG. 1. The reflectivity of cadmium fluoride. The circles represent measured data points. The solid curve is a least-squares fit of the data to a single classical dispersion oscillator form.

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[1] The stable low-temperature form of PbF_2 is an orthorhombic form, see H. Swanson, Natl. Bur. Std. (U. S.), Circ. No. 539. When grown as described above from the melt, the metastable cubic form persists to room temperature. See Ref. 5.

[2] J. S. Prener and J. D. Kingsley, J. Chem. Phys. **38**, 667 (1963).

[3] J. S. Prener and J. D. Kingsley, J. Chem. Phys. **35**, 2256 (1961).

[4] D. A. Jones, R. V. Jones, and R. W. H. Stevenson, Proc. Phys. Soc. (London) **B65**, 906 (1952).

[5] D. A. Jones, Proc. Phys. Soc. (London) **B68**, 165 (1955). The refractive-index measurements between 0.7 and 0.4 μ given in this paper can be fit quite well to a classical dispersion expression $n^2-1=c[1-(\lambda_0/\lambda)^2]^{-1}$ with $c=1.987$ and $\lambda_0=0.1480$ μ.

[6] W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, Phys. Rev. **127**, 1950 (1962).

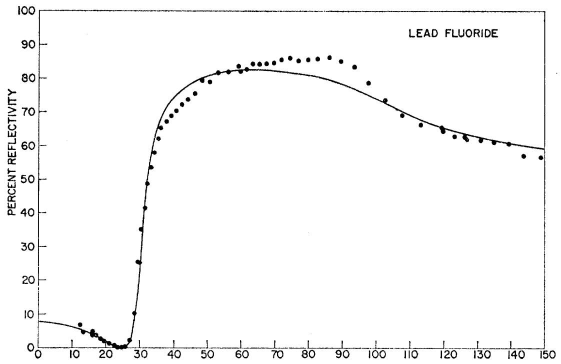

FIG. 2. The reflectivity of lead fluoride. The circles represent measured data points. The solid curve is a least-squares fit of the data to a single classical oscillator form.

measurement of the reflected energy, this information can be recovered through the use of the dispersion integral[7]

$$\theta(\omega)=\frac{2\omega}{\pi}\int_0^{\omega_m}\frac{\ln[R(\omega')/R(\omega)]^{1/2}}{\omega^2-\omega'^2}d\omega'. \tag{2}$$

In the present case, the limits of the integral cause no undue concern, since both well below and well above the characteristic lattice frequencies the reflectivity approaches constant limiting values. (The frequency ω_m is chosen to be large compared to ionic frequencies and small compared to electronic frequencies.) However, the minimum in the immediate vicinity of the short-wavelength side of the reststrahl band is troublesome because there is insufficient reflected energy to obtain accurate measurements. On the other hand the behavior of the reflectivity in this region does make an important contribution to the integral.[7] These minima result from a matching of the real refractive index of the medium with that of air (i.e., $n=1$), so that the only optical mismatch of the boundary is due to k, which is quite small in this region. In this work the following expedient was employed. As is well known, the dielectric response of a lattice with $\mathfrak{M}$ optically active modes can in many cases be approximated quite well by an expression of the type

$$\epsilon=\epsilon_e+\sum_{j=1}^{m} S_j\omega_j^2/\omega_j^2-\omega^2+i\omega\gamma_j\,, \tag{3}$$

i.e., by sums of classical oscillator dispersion terms. The results of a least-squares fit of such a relation (with $m=1$) to the reflectivity data for CdF_2 and PbF_2 are also shown on the respective figures. The frequency distribution of data points weights the fit to the short-wavelength edge of the reststrahl. Reflectivities calculated from these expressions were then used to supplement the measured points in the immediate vicinity of the minimum. The numerical integration and calculation of the subsidiary dielectric properties was programmed for an IBM-7090 digital computer. The values for the real and imaginary dielectric response that result are given in Figs. 3 and 4. The actual data points were used as input rather than smoothed values, and the scatter in the results give some indication of their accuracy. A check on the reliability of the computation procedure was made by computing the optical constants from hypothetical reflectivity data derived from Eq. (3) with constants appropriate to CaF_2. A comparison of these results with those calculated directly from Eq. (3) indicated an rms deviation of $<5\%$, the relative deviations being greatest in the regions where ϵ'' is small.

III. DISCUSSION

As is the case for all fluorite lattices investigated thus far, the dielectric responses of CdF_2 and PbF_2 have

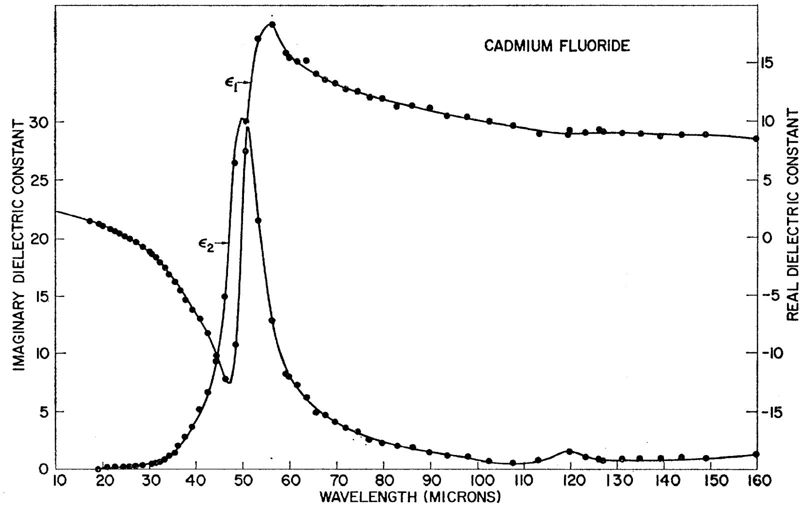

FIG. 3. The infrared dielectric response of cadmium fluoride as derived from the KK analysis of the reflectivity.

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[7] F. Stern, in *Solid State Physics* (Academic Press Inc., New York, 1963), Vol. 15, p. 333.

only one strong resonance. This is readily understood by group-theoretical arguments which indicate that at $k=0$ the "group of k" is O_h ($m3m$) and the displacements of the three atoms in the unit cell transform as $2F_{1u}+F_{2g}$. The triply degenerate F_{2g} states are Raman active, and one of the F_{1u} representations corresponds to the three acoustic branches. The degeneracy of the remaining F_{1u} states is partially lifted by the macroscopic electric field associated with the longitudinal mode. The remaining twofold degenerate mode has transverse polarization components which interact with the radiation field in first order.

A careful analysis of the nature of this interaction is necessary to discuss the form of the dielectric response. Recent treatments of this problem are in essential agreement that in real physical systems the functional form of Eq. (3) is preserved but that the damping factor, instead of being constant is itself frequency dependent.[8] This can result in not only a finite breadth in the main resonance(s) but also in the appearance of subsidiary peaks or side bands in the imaginary dielectric response. Such effects are well known and can be ascribed to processes involving the creation (or simultaneous creation and destruction) of two or more phonons through the intermediate virtual excitation of the $k=0$ transverse-optic (TO) mode. Considerations of this sort suggest that it would be of interest to use the real and imaginary dielectric response derived from the *KK* relation to evaluate the experimental damping functions defined by

$$\gamma(\omega)=[\epsilon''/(\epsilon'-\epsilon_e)][(\omega_0^2-\omega^2)/\omega]; \tag{4}$$

Figs. 1 and 2 show the results for CdF_2 and PbF_2. Included is the rms probable error for an assumed error in ϵ' and ϵ'' (10% or 0.1, whichever is largest). Although the uncertainty in the points is great, particularly far removed from the resonance, what should constitute regions of secondary absorption show up as peaks in the damping functions. (Treating in the same manner data taken on CaF_2, the damping function shows quite clearly an increase at $\sim 30\,\mu$ which corresponds to the subsidiary weak resonance (10% of the fundamental-mode strength) assumed by Kaiser *et al.*[6] as well as a long-wavelength behavior similar to that seen in CdF_2.) These curves should reflect the combined density of states of phonon pairs which couple with the $\mathcal{K}=0$ TO mode, and as such should be re-examined when more is known about the phonon dispersion in these materials.

It is possible to extract information concerning the longitudinal-optical branch as well as the transverse ones directly from the dielectric response, but some care is necessary in the definition of terms when there is damping present. This point has recently been discussed by Barker.[9] Formally the longitudinal and transverse eigen-frequencies are given by the roots and poles, respectively, of the dielectric response function, but for a functional form such as Eq. (3) these frequencies are displaced an amount $i\gamma/2$ from the real frequency axis. From an experimental point of view, the frequencies $\omega_\pm$ where $\epsilon'(\omega)=0$ are well defined and can be related to the real part of the eigen-frequencies above, which we shall refer to as ω_{LO} and ω_{TO}. Using Eq. (3), a short analysis shows that to first order in an expansion in $(\gamma/\omega_0)^2$,

$$\omega_{LO}^2=\omega_+^2-\{\tfrac{1}{4}-\epsilon_s/(\epsilon_s-\epsilon_e)\}\gamma^2, \tag{5}$$

$$\omega_{TO}^2=\omega_-^2-\{\tfrac{1}{4}+\epsilon_e/(\epsilon_s-\epsilon_e)\}\gamma^2. \tag{6}$$

We have used Eqs. (5) and (6) in connection with the experimental data of Figs. 5 and 6 to determine the eigen-frequencies. As Barker shows,[9] the Lyddane-Sachs-Teller (LST) relation for a system with damped dielectric response involves the magnitudes of the

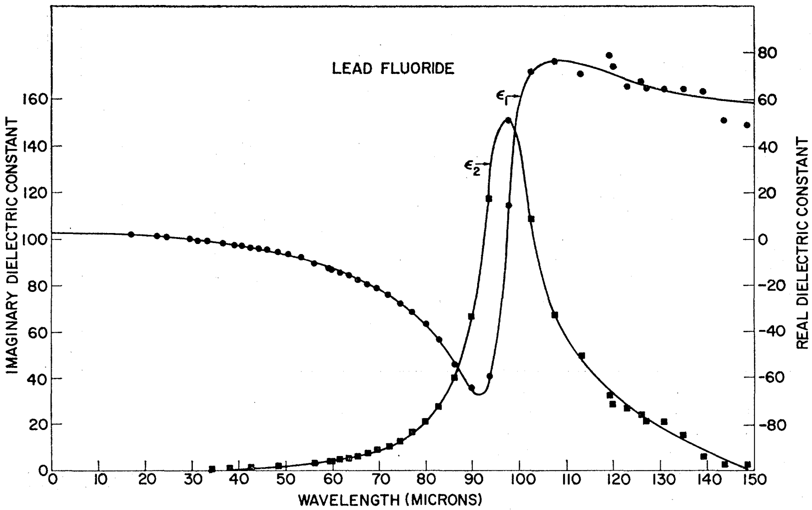

FIG. 4. The infrared dielectric response of lead fluoride as derived from the *KK* analysis of the reflectivity.

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[8] See, for example, M. Lax, J. Phys. Chem. Solids **25**, 487 (1964).

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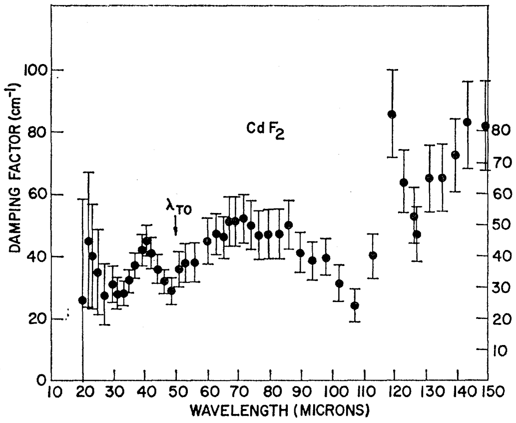

FIG. 5. The frequency-dependent damping function $\gamma(\omega)$ for cadmium fluoride as derived from Eq. (4). λ_{TO} indicates the wavelength corresponding to the resonance frequency.

complex frequencies rather than the real parts, i.e.,

$$\epsilon_s=[(\omega_{LO}^2+\tfrac{1}{4}\gamma^2)/(\omega_{TO}^2+\tfrac{1}{4}\gamma^2)]\epsilon_e. \tag{7}$$

Although Eqs. (5)-(7) are derived for a system with constant damping, we assume them to be approximately correct for frequency-variable damping also since $\gamma(\omega)$ is a slowly varying function. We have also derived by numerical integration from the computed values of the imaginary dielectric constant the total infrared contribution to the real dielectric constant,

$$\epsilon_s-\epsilon_e=(2/\pi)\int_0^{\omega_m}\epsilon_2(\omega)\omega^{-1}d\omega. \tag{8}$$

The use of Eqs. (7) and (8) allows us to deduce values of ϵ_s and ϵ_e which can be compared with directly measured values. This is done in Table I. Two remarks can be made concerning the agreement. The measured static value for CdF$_2$ is certainly too high. In our samples the value doubles on lowering the frequency from 100 to 10 kc/sec, and is accompanied by a high loss tangent at both frequencies. We hope to investigate the cause of this spurious low-frequency dispersion in more detail. The discrepancies between the calculated and observed high-frequency dielectric constants are harder to explain away. In the case of CdF$_2$ the measured value is uncorrected for whatever electronic dispersion is present at the visible wavelengths used for the measurements. The PbF$_2$ data has been corrected for this however,[5] and a discrepancy of nearly 20% remains. Our determination of $(\omega_{LO}/\omega_{TO})^2$ for CaF$_2$ agrees with that determined directly by inelastic neutron scattering to within 6%. Assuming the neutron data is the more correct and that this relative error characterizes the CdF$_2$ and PbF$_2$ data also, it appears that at least in PbF$_2$ some inadequacy of the LST relation may exist over and above the errors involved in the measurements. In any case we recommend (and use in what follows) as most nearly correct the calculated static values and the measured high-frequency values.

TABLE I. Some quantities related to the infrared optical properties of CdF$_2$ and PbF$_2$. The transverse and longitudinal eigen-frequencies were derived from the measured dielectric response with slight corrections due to Eqs. (5) and (6). The calculated values of the static (ϵ_s) and high-frequency (ϵ_e) dielectric constants result from Eqs. (7) and (8). The effective charge $Z'(F)$ given in atomic units is calculated from Eq. (9). The effective charge on the metal ion is $-2Z'(F)$.

	CdF$_2$	PbF$_2$
ω_{TO} (cm^{-1})	202	102
ω_{LO} (cm^{-1})	384	337
ϵ_s (calc)	8.09	27.4
ϵ_s (meas)	<9.4	26.3
ϵ_e (calc)	2.23	2.51
ϵ_e (meas)	2.40[a]	2.99[b]
$-Z'(F)$	0.795	0.873

[a] Reference 4. [b] Reference 5.

One final interesting set of parameters we are able to extract from our work is the effective charge. In producing the polarization of the lattice due to their displacement, the ions behave as if they carried an effective charge Z_i' which differs more or less from the actual net charge (inasmuch as the charges can be uniquely assigned to ions) by distortion effects.[10] The strength of the dielectric response is a measure of this polarization, and for a fluorite lattice the effective charges are given by[11]

$$\begin{aligned}-Z_M'Z_F'&=2(Z_F')^2\\&=(9v/4\pi e^2)[(\epsilon_s-\epsilon_e)/(\epsilon_e+2)^2]\mu\omega_{TO}^2,\\ \mu&=[m_Mm_F/(m_M+2m_F)],\end{aligned} \tag{9}$$

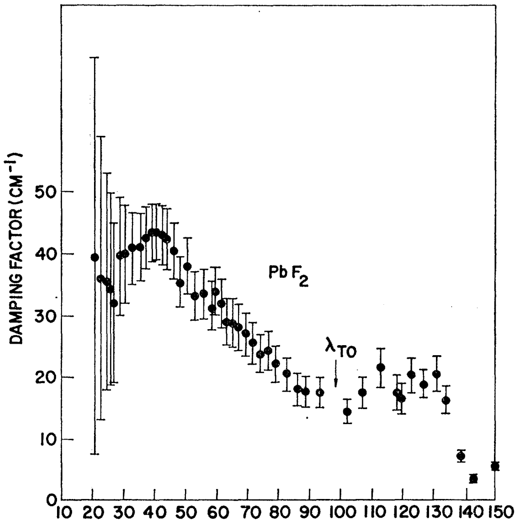

FIG. 6. The frequency-dependent damping function $\gamma(\omega)$ for lead fluoride.

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[10] B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950).

[11] J. D. Axe, following paper, Phys. Rev. **139**, A1215 (1965).

where v is the unit cell volume. The values obtained for CdF$_2$ and PbF$_2$ are given in Table I. The values are not very different than those found for the alkaline-earth halides where almost certainly the net charges are the full ionic values.[11] A crude estimate of the distortion effects on the basis of the shell model shows (1) the greater effective charge for PbF$_2$ reflects not so much greater ionicity but the greater polarizability of the Pb^{2+} ion as compared to the Cd^{2+} ion; (2) the net ion charges must be about 90% of the full ionic values in both cases. This latter conclusion is probably consistent with the observation that the lattice energies of CdF$_2$ and PbF$_2$ differ by less than 10% from that calculated using a Madelung attractive potential with full ionic charges.[12]

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Long-Wave Lattice Dynamics of the Fluorite Structure*

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A simple shell model is used to calculate expressions for the long-wavelength vibrational eigenfrequencies and elastic constants of the fluorite (CaF$_2$ type) lattice. The concept of effective charge is introduced and expressions analogous to the Szigeti relations for lattices with diatomic unit cells are given. These and other relations between the acoustic and optical properties derived for the dipole shell model are in better agreement with the measured properties of the alkaline-earth fluorides than are those derived for a rigid-ion model. The large deviation from the Cauchy relation $C_{12}=C_{44}$ seems to be largely explainable in terms of the shell-model correction to the internal strain.

I. INTRODUCTION

RECENT experimental studies of lattice dynamics, much of it in the form of inelastic slow-neutron scattering,[1,2] have made abundantly clear certain shortcomings in what may be termed the rigid-ion model of a crystal lattice which evolved from the work of Born and others.[3–5] This model, in which nonpolarizable ions interact through long-range electrostatic and short-range repulsive forces, explains reasonably well many properties of simple ionic crystals (e.g., cohesive energies, elastic constants, Debye temperatures), but is quite inadequate in discussing dielectric properties and the detailed dispersion relations of (particularly) longitudinal modes. Of the various attempts to introduce the feature of polarizability correctly into lattice dynamics (complicated by the fact that in addition to being electrically polarizable, ions are also mechanically polarized by the motions of their neighbors[6]), the shell model, introduced in various forms by several workers[7–10] and developed and formalized by Cochran[11] and Cowley,[12,13] has received the most attention recently. Although the theory has limitations, it is physically appealing and even in its simplest form does much to alleviate the discrepancies noted above in simple ionic structures (NaI, KBr)[14] as well as more homopolar ones (Ge, GaAs).[15,16]

Materials having the fluorite structure, only modestly more complicated than the rock-salt or diamond structures mentioned above, are numerous, and experimental data, much of it recent, on the elastic and optical properties of fluorite (CaF$_2$) and structurally related

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