justifiable set of parameters from vapor data gives the worst account of the crystal. Furthermore, agreement of our calculations with observation is not nearly as good for neon as for argon. Of course, the odd-derivative anharmonic effects that we have omitted may be much more significant for the lighter element, but this is not likely to account fully for the apparent relative inadequacy of the Lennard-Jones form in the case of neon. We also feel that a good case can be made, both by inference from the work presented here and from first-principles considerations, that the potential parameters change on going from the gas phase to the crystal. This point of view is an alternative in that it would then have to regard the fairly satisfactory consistency in the case of argon as partially accidental. The possibility of shifts in the Lennard-Jones potential between phases is not entirely the same thing as the possibility of "three-body forces,"[32] although there certainly are aspects of similarity, because three-body forces in the usual sense imply a noncentral effective interaction between atom pairs. Strictly speaking, of course, a local, instantaneous, central potential can only be an approximation to the true forces between atomic nuclei, which are given at the most fundamental level by the Coulomb potential shielded by the full nonlocal retarded electronic dielectric function.

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[32] L. Jansen, Phys. Rev. 135, A1292 (1964).

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Temperature and Pressure Dependence of the Dielectric Constants of the Thallous Halides*

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The effects of temperature (76–400°K) and hydrostatic pressure (up to 20 kbar) on the static dielectric constants of single crystal TlCl and TlBr and polycrystalline TlI were investigated. TlCl and TlBr have the CsCl structure, whereas TlI transforms from an orthorhombic structure to the CsCl structure at 4.8 kbar and 300°K. In all cases, the dielectric constant ϵ decreases with both increasing temperature (at low temperatures) and increasing pressure. At 1 bar and 293°K, $(\partial \ln \epsilon/\partial T)_P$ and $(\partial \ln \epsilon/\partial P)_T$ (in units of 10^{-4}°K^{-1} and 10^{-2} kbar^{-1}) are -3.94 and -1.81, -3.70 and -1.77, -0.68 and -0.65 for TlCl, TlBr, and TlI (orthorhombic), respectively. For TlI (cubic) the corresponding values at 3 kbar and 293°K are -4.04 and -1.47. At the orthorhombic $\rightarrow$ cubic transition, ϵ of TlI increases by 35%, but this change is found to be entirely due to the change in volume, the total polarizability per molecule being independent of crystal structure. The temperature dependence of ϵ is separated into volume-dependent and volume-independent contributions. For the thallous halides the latter contribution, which is determined by anharmonic lattice effects, is large and determines the sign of $(\partial \ln \epsilon/\partial T)_P$. On the basis of Szigeti's theory and the assumption that the optical dielectric constant ϵ_{op} is a unique function of volume, it is found that anharmonicities in the potential energy and nonlinearities in the dipole moment account for 30–40% of the lattice contribution to ϵ of the thallous halides. The effective charge ratio e^*/e at room temperature is 0.96 for TlCl and 0.95 for TlBr. At low temperatures, ϵ of TlCl and TlBr obeys a Curie-Weiss law $\epsilon = c/(T-T_0)$ with T_0 negative. At high temperatures (>300°K) the dielectric constant and dielectric loss are predominantly determined by the formation and transport of lattice defects. The activation energies calculated from the results agree well with values obtained from ionic-conductivity measurements.

I. INTRODUCTION

THIS paper deals with the effects of temperature (76 to 400°K) and hydrostatic pressure (up to 20 kbar) on the static dielectric constants of the three thallous halides TlCl, TlBr, and TlI. A knowledge of the dielectric constants of ionic crystals and their temperature and volume (or pressure) dependences is of considerable interest because the dielectric constant enters into the theoretical treatment of various physical properties, e.g., the theories of electron-phonon interactions and infrared dispersion and effective field considerations. In addition, the temperature and pressure dependences of the dielectric constant combined with a knowledge of the thermal expansion coefficient and compressibility make it possible to separate the temperature dependence of the dielectric constant at constant pressure into its volume-dependent and volume-independent contributions. As will be discussed later, the latter contributions are determined completely by anharmonic lattice effects.

The thallous halides are a particularly interesting group of compounds to study. Unlike most ionic crystals which exhibit an increase of dielectric constant with increasing temperature at low temperatures, the dielectric constants of the thallous halides decrease with in-

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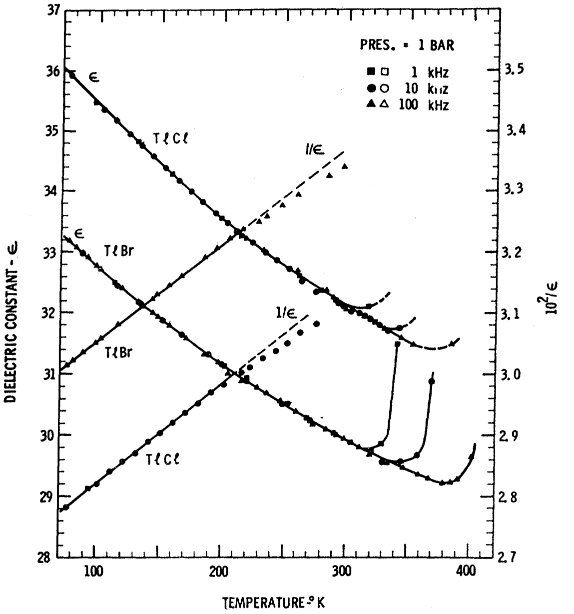

FIG. 1. The temperature dependence of the static dielectric constant and its reciprocal for TlCl and TlBr.

creasing temperature. Of the three compounds, TlCl and TlBr crystallize in the simple cubic CsCl type structure. TlI, on the other hand, crystallizes in a double-layered orthorhombic (C_{mcm}-D_{2h}^{17}) structure with a coordination number of seven. It transforms to the high temperature CsCl structure with both increasing temperature (170°C at 1 bar) and pressure (4.8 kbar at 25°C). The details of the transformation have been recently reported elsewhere.[1] This transformation permits a study of the effects of crystal structure on the dielectric constant.

The temperature dependence of the dielectric constants ϵ of TlCl and TlBr at atmospheric pressure have been previously reported. Lowndes[2] reported the values of ϵ of both compounds at 1.5, 90, and 290°K. Rao and Smakula[3] reported the temperature dependence of ϵ of TlCl over the range 4–600°K. The temperature and pressure derivatives of ϵ of TlBr were reported by Havinga and Bosman.[4] There appear to be no previously reported measurements on TlI except for a brief account of the temperature dependence of ϵ.[3]

In the present work, a detailed investigation of the effects of temperature and pressure on the dielectric constant and dielectric loss of TlCl, TlBr, and TlI was carried out. The measurements were made at 1, 10, and 100 kHz. A brief description of the experimental techniques is given in Sec. II. The results are presented in Sec. III and discussed in Sec. IV. First, we discuss the temperature and frequency dependence of the dielectric constant and dielectric loss at high temperatures where the formation and relaxation of lattice defects become the predominant effects. We then evaluate the various contributions to the temperature dependence of ϵ and relate these to the theoretical treatment of each contribution. This is followed by an evaluation of the anharmonic contribution to the dielectric constant and of the effective charge. Finally, the Curie-Weiss behavior of the dielectric constant at low temperatures and its possible relation to the theory of ferroelectricity are discussed. Section V summarizes the results and conclusions.

II. EXPERIMENTAL TECHNIQUES

The samples used were in the form of thin plates 0.5–1.0 mm thick and 0.70–1.50 cm² in area. Measurements were made on at least two samples of each material. The TlCl and TlBr samples were single crystals oriented with the smallest dimension along one of the cube axes. Two types of samples of TlI were used. The first type consisted of plates cut from a boule grown at this laboratory by the Bridgman-Stockbarger technique. As grown, this boule was a single crystal; however, upon cooling it transformed from the cubic to the orthorhombic phase resulting in a polycrystalline mass with some preferred orientation. The other TlI samples were fused powder pellets (99% of theoretical density) prepared by a hydrostatic compacting technique under a pressure of 11 kbar. The starting material for both types of samples was the same. Attempts to grow TlI crystals from solution yielded only very small crystals not suitable for the present experiments. Silver electrodes painted on the large faces of the samples were used for both the temperature and pressure measurements. There was no evidence of any silver diffusion into the samples.

The pressure experiments were performed in a 30-kbar hydrostatic apparatus using a 50–50 mixture of *n*-pentane and iso-pentane as pressure fluid. The fluid was passed through silica gel to remove any traces of water. A description of the apparatus and general experimental procedures, including pressure calibration, has been given elsewhere.[5] Pressure was measured to an accuracy of better than ±1%.

The temperature dependence of the dielectric constant was measured at atmospheric pressure in a cell in which sample temperature was controlled by a stream of dry nitrogen or helium gas. The temperature dependence of the dielectric constant of the cubic phase of TlI was measured under pressure using the techniques described earlier.[5] Temperature change was measured to an accuracy of ±0.1°C.

Sample capacitance was measured at 1, 10, and 100 kHz using a General Radio Model 1615A transformer ratio arm bridge with three terminal connections and

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[1] G. A. Samara, L. C. Walters, and D. A. Northrop, J. Phys. Chem. Solids **28**, 1875 (1967).

[2] R. P. Lowndes, Phys. Letters **21**, 26 (1966).

[3] K. V. Rao and A. Smakula, J. Appl. Phys. **36**, 3953 (1965). See also A. von Hippel, *Dielectric Materials and Applications* (John Wiley & Sons, Inc., New York, 1954), p. 373.

[4] E. E. Havinga and A. J. Bosman, Phys. Rev. **140**, A292 (1965); **129**, 1593 (1963).

[5] G. A. Samara, J. Phys. Chem. Solids **26**, 121 (1965).

having an accuracy greater than 0.1%. Shielded leads and sample holders were used. These techniques eliminate stray capacitance effects.

The dielectric constant and its change with temperature and pressure were calculated from the measured sample capacitance, C, by correcting for changes in sample dimensions due to thermal expansion and compression. For isotropic samples, it is easily shown that the relations are

$$(1/\epsilon_0)(\partial\epsilon/\partial T)_P=(1/C_0)(\partial C/\partial T)_P-(1/3V_0)(\partial V/\partial T)_P, \quad (1)$$

and

$$(1/\epsilon_0)(\partial\epsilon/\partial P)_T=(1/C_0)(\partial C/\partial P)_T-(1/3V_0)(\partial V/\partial P)_T. \quad (2)$$

ϵ_0, C_0 and V_0 are the values of the dielectric constant, capacitance, and volume at atmospheric pressure and temperature. The compressibility data used were taken from Bridgman[6] for TlCl and TlBr and from our recent measurements[1] for TlI. The volume expansion data for TlCl and TlBr were taken from the literature[7,8] while our data[1] for TlI were used. These data are available only above room temperature, and the thermal expansion coefficients were assumed to be constant down to 76°K. The observed linearity[1] of the variation with temperature of the lattice parameters of TlI over a wide temperature range indicates that the error introduced by this extrapolation should be small.

III. RESULTS

Figure 1 shows the effects of temperature on the dielectric constants of TlCl and TlBr at atmospheric pressure. Below 300°K, ϵ decreases with increasing temperature and is independent of frequency over the frequency range covered; however, at high temperatures ϵ increases exponentially with increasing temperature and is strongly frequency-dependent.

The results for the orthorhombic phase of TlI (Fig. 2) are qualitatively similar to those in Fig. 1; however, the temperature coefficient at low temperatures is up to an order of magnitude smaller than those for TlCl and TlBr. There are also quantitative differences in the values of ϵ and $(\partial\epsilon/\partial T)_P$ between the fused powder sample and that cut from the boule (henceforth labeled "crystal"). These differences can be attributed to the facts that the density of the fused powder sample was only 99% of theoretical density and the x-ray patterns of the "crystal" sample showed some preferred orientation. Anisotropies in ϵ in the orthorhombic phase can be expected in view of the fact that the linear thermal expansions of this phase are highly anisotropic.[1]

The changes in capacitance with temperature for the TlI samples in the orthorhombic phase were quite small and, therefore, the calculated changes in ϵ reflect mostly changes in sample dimensions (i.e., the $(1/3V_0)(\partial V/\partial T)_P$ term in Eq. 1). Since, as mentioned in Sec. II, it was assumed in the calculations that the volume expansion coefficient is constant between 293 and 76°K, the accuracy of the results below room temperature in Fig. 2 depends on the validity of this assumption. In view of this, we give in Table I the fractional change in sample capacitance at 20-degree intervals for the TlI as well as the TlCl and TlBr samples. These values will allow the recalculation of ϵ more accurately when low-temperature thermal-expansion data become available.

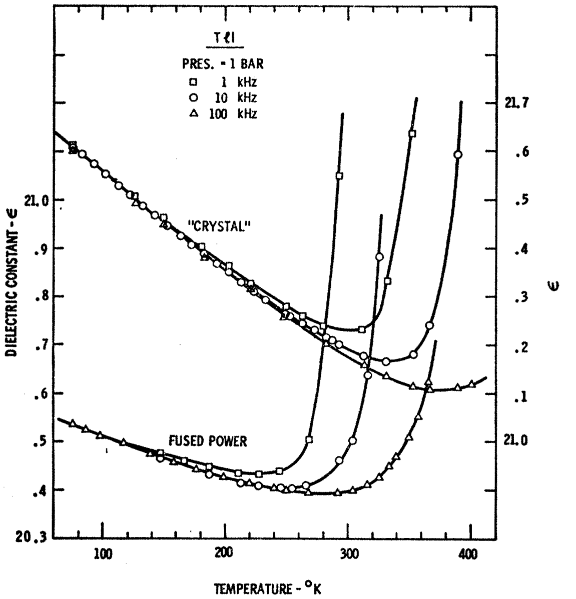

FIG. 2. The temperature dependence of the static dielectric constant of TlI. The fused powder data are read against the left-hand ordinate and the "crystal" data against the right-hand ordinate.

Table II gives the values of ϵ and $(\partial \ln\epsilon/\partial T)_{1\text{ bar}}$ for the three compounds and compares the results with literature values. There appear to be no previously reported detailed data on the temperature dependence of

TABLE I. Fractional change of the capacitance of the thallous halides measured at 1 bar. Here $\Delta C=C_T-C_{293°\text{K}}$.

T (°K)	TlCl	TlBr	TlI[a] ("Crystal")	TlI[a] (Fused Powder)
	$\Delta C/C_{293°\text{K}}$			
293	0	0	0	0
280	0.0042	0.0041	0.00040	−0.00052
260	0.0115	0.0107	0.00105	−0.00133
240	0.0195	0.0178	0.00176	−0.00195
220	0.0281	0.0254	0.00254	−0.00238
200	0.0370	0.0335	0.00340	−0.00266
180	0.0465	0.0421	0.00438	−0.00279
160	0.0565	0.0513	0.00540	−0.00284
140	0.0670	0.0610	0.00645	−0.00283
120	0.0777	0.0712	0.00755	−0.00277
100	0.0890	0.0820	0.00870	−0.00270
80	0.1003	0.0930	0.00990	−0.00259

[a] Orthorhombic phase.

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[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 21 (1940).

[7] P. G. Hambling, Acta Cryst. 6, 98 (1953).

[8] R. S. Krishnan, *Progress in Crystal Physics* (S. Viswanathan, Madras, 1958), Vol. I, p. 26.

TABLE II. The static dielectric constant ϵ of the thallous halides at 1 bar and 20°C and its initial temperature and pressure derivatives. Present results are compared with literature values, where the latter are available.

Compound	ϵ	$10^4\times\left(\frac{\partial\ln\epsilon}{\partial T}\right)_{1\text{ bar}}$ $(°\text{K})^{-1}$		$10^2\times\left(\frac{\partial\ln\epsilon}{\partial P}\right)_{20°\text{C}}$ $(\text{kbar})^{-1}$	
		This work	Others	This work	Others
TlCl	32.2 ± 0.2	-3.94 ± 0.05	≈-4[a]	-1.81 ± 0.05	
TlBr	30.0 ± 0.2	-3.70 ± 0.05	-3.1[b]	-1.77 ± 0.05	-1.78[b]
TlI (ortho.)	21.2 ± 0.2	-0.68 ± 0.05		-0.65 ± 0.05	
TlI (cubic)	29.6 ± 0.5	-4.04 ± 0.10[c]		-1.47 ± 0.10	

[a] Estimated from data in Ref. 3. [b] Reference 4. [c] Evaluated at 3 kbar.

ϵ of TlI. The curve reported by von Hippel[3] on pressed powder shows practically no change of ϵ with temperature above room temperature at 10 MHz. Roa and Smakula[3] remarked that the "orthorhombic modification of TlI has positive temperature coefficient of ϵ." However, no data were given and no mention was made of the frequency and temperature range of the measurements nor the type of sample used. As seen from Fig. 2, a positive temperature coefficient of ϵ is observed at and above room temperature especially in the case of fused powder samples. In this temperature range the dielectric loss $\tan\delta$ increases rapidly with increasing temperature. As will be discussed in Sec. IV, this increase in ϵ and $\tan\delta$ is caused by dipolar contributions associated with the formation and activation of lattice defects.

The pressure dependences of ϵ of TlCl and TlBr at room temperature are given in Fig. 3. Table II gives the initial derivatives $(\partial\ln\epsilon/\partial P)_T$. The value for TlBr is in good agreement with that reported by Havinga and Bosman.[4]

Figure 4 shows the effects of pressure on the dielectric constant of TlI. In both phases, ϵ decreases monotonically with increasing pressure, but the rate of decrease in the orthorhombic phase is only about half that of the cubic phase. The results of the fused powder and "crystal" samples were quite similar; however, it is felt that those of the "crystal" are more representative of the intrinsic behavior of the material because at the temperature of the measurements (295°K) ϵ of the fused powder is strongly frequency-dependent (see Fig. 2). The increase in ϵ at the transition $\Delta\epsilon$ varies somewhat from sample to sample. The average increase for six samples is $(35.0\pm2.5)\%$. The dimensions of the different samples most likely do not change in exactly the same way at the transition, thus accounting, at least in part, for the observed variation in $\Delta\epsilon$.

In the cubic phase of TlI, $1/\epsilon$ is very nearly a linear function of pressure as shown in Fig. 4. From an extrapolation of this linear relation to zero pressure we get for ϵ and $(\partial\ln\epsilon/\partial P)_T$ of this phase at 1 bar and 295°K the values 29.6 ± 0.5 and $-(1.47\pm0.10)\times10^{-2}$

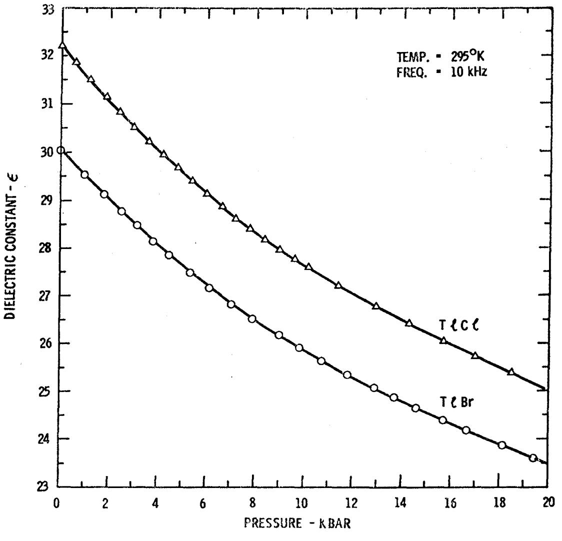

FIG. 3. The pressure dependence of the static dielectric constant of TlCl and TlBr.

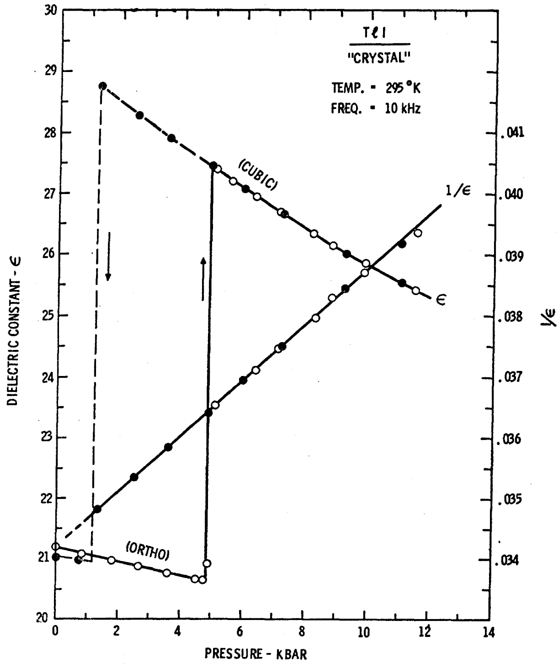

FIG. 4. The pressure dependence of the static dielectric constant of TlI showing the discontinuity at the orthorhombic-cubic transition and the hysteresis effect. The linear pressure dependence of the reciprocal of the dielectric constant in the cubic phase is also shown. Open and closed circles represent data taken with increasing and decreasing pressure, respectively.

TABLE III. The activation energies of the thallous halides at 1 bar obtained from dielectric loss measurements at high temperatures. Present results are compared with literature values obtained from ionic-conductivity measurements.

			E (eV)		
			TlI (ortho.)		TlI (cubic)
	TlCl	TlBr	"Crystal"	Fused powder	"Crystal"
This work	0.84±0.05	0.85±0.04	0.62±0.04	0.48±0.03	≈0.50[a]
Lehfeldt[b]	0.79±0.03	0.80±0.05			
Others[c]	0.75 to 0.87	0.75 to 0.84			

[a] Evaluated at 3 kbar. [b] Reference 11. [c] Values quoted in Ref. 11.

kbar^{-1}, respectively. These values are listed and compared with the corresponding values for TlCl and TlBr in Table II. They obey the general trend for the three halides.

The temperature dependence of ϵ of the cubic phase of TlI was measured at 3 kbar. It was desirable to make this measurement at a fairly low pressure because the thermal expansion data for this phase were available only at 1 bar. At 1 bar, the transition from the orthorhombic to the cubic phase occurs at 170°C, but at this and higher temperatures, ϵ at low frequencies increases exponentially with temperature because of the formation of lattice defects (see Sec. IV). Measurements at 3 kbar are possible only because of the large pressure hysteresis of the transition (Fig. 4). Data at 10 and 100 kHz gave, within experimental error, the same value of the coefficient $(\partial \ln\epsilon/\partial T)_P$ which at 20°C is $-(4.04\pm0.10)\times10^{-4}$°K^{-1}. As seen from Table II, this value is comparable to those of TlCl and TlBr evaluated at 1 bar.

IV. DISCUSSION

A. Frequency and Temperature Effects

The dielectric constant of a substance is generally determined by four main contributions: (1) electronic polarization, (2) lattice or infrared polarization, (3) dipolar polarization associated with either permanent dipoles (not present in the thallous halides) or dipoles produced by impurities and lattice defects, and (4) space-charge polarization. These contributions are not completely independent; however, they exhibit different frequency response. At very low frequencies all four contributions are important, whereas at optical frequencies only the electronic polarization comes into play. In the present work, we are concerned with frequencies orders of magnitude smaller than the reststrahl frequencies and, therefore, the frequency and temperature dependence of the dielectric constant observed at high temperatures (see Figs. 1 and 2) must be caused by contributions (3) and (4). Both associated and unassociated defects probably play an important role. The concentration of defects N increases exponentially with temperature[9] as

$$N=N_0\exp(-E_d/kT), \tag{3}$$

where N_0 is a constant and E_d is the energy of formation of defects. The relaxation of defects, on the other hand, decreases with increasing temperature, the relaxation time τ being generally expressed in the form

$$\tau=\tau_0\exp(U/kT), \tag{4}$$

where τ_0 is the time constant of natural lattice vibrations and U is the energy barrier separating two equivalent positions of a defect.

At high temperatures, the dielectric constant and the dielectric loss, tanδ, of the three thallous halides studied increase exponentially with increasing temperature and decrease with increasing frequency. In this temperature region the dielectric loss is dominated by the conductivity of the sample. The relationship is[10]

$$\tan\delta=\epsilon''/\epsilon'=4\pi\sigma/\epsilon'\omega, \tag{5a}$$

where

$$\sigma=\sigma_0\exp(-E/kT). \tag{5b}$$

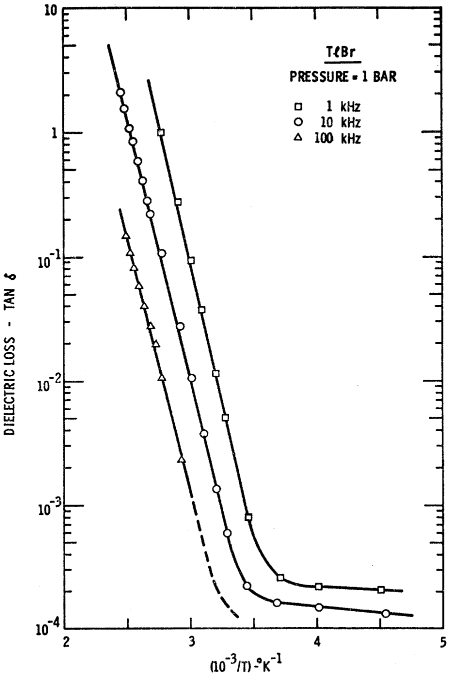

FIG. 5. The temperature dependence of the dielectric loss of TlBr. In the high-temperature region tanδ is proportional to the conductivity.

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[9] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1960), p. 477.

[10] See e.g., A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

Here ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant, ω is the angular frequency, σ is the dc conductivity, σ_0 is a constant, and E is the activation energy. In the intrinsic range, E is given approximately by $E=E_a+\frac{1}{2}E_d$ where E_a is the activation energy for motion of defects and E_d is the energy of formation of defects.[9] It is thus of interest to compare the activation energies obtained from the present results with those obtained from ionic-conductivity measurements, where the latter are available.

Figure 5 shows a plot of log tanδ versus $1/T$ for TlBr at three frequencies. At high temperatures the results exhibit the expected linear behavior with the slopes very nearly independent of frequency. The TlCl and TlI results are similar. Table III summarizes the activation energies obtained from the slopes of the linear portions of the curves at high temperatures. Lehfeldt[11] has measured the ionic conductivities of TlCl and TlBr at atmospheric pressure. His results show a linear dependence of logσ versus $1/T$ from about room temperature up to the melting points. His activation energies are compared with ours in Table III which also lists earlier results quoted by Lehfeldt. The agreement is good. There is also good agreement between the value of the conductivity calculated from Eq. (5a) and Lehfeldt's results.

In the orthorhombic phase of TlI, E for the "crystal" is about 30% larger than that for the fused powder. A number of factors may be responsible for this difference. We have mentioned earlier that in the "crystal" there was some preferred orientation, and the fused powder was only 99% of theoretical density. Also, the mechanism for diffusion in the powder is probably different than that in the "crystal" due to the influence of grain boundaries and other imperfections. The value of E for the cubic phase of TlI was determined from measurements at 3 kbar. It is based on the results of only one experiment at temperatures up to 100°C, and should therefore only be considered as an approximate value.

At low temperatures the effects of crystal defects[12] become negligible, and the dielectric constant is then determined by optical and infrared contributions. This is the situation in the frequency-independent regions of Figs. 1 and 2. The remainder of our discussion will deal with the behavior of the dielectric constant in this region.

B. Contributions to the Temperature Dependence of the Dielectric Constant—Macroscopic Treatment

A microscopic theory relates the dielectric constant of ionic crystals to the electronic and ionic polarizabilities of each ion and to their interaction. Therefore, a discussion of the temperature dependence of the dielectric constant necessarily entails a knowledge of the temperature dependence of the individual polarizabilities. Such information is not available. It is nevertheless instructive to treat the results on a macroscopic scale.

For a cubic or isotropic material, the macroscopic Clausius-Mossotti relationship

$$(\epsilon-1)/(\epsilon+2)=(4\pi/3)(\alpha/V)\,, \tag{6}$$

holds.[4,13] Here α is the total polarizability of a macroscopic small sphere of volume V. The logarithmic derivative of Eq. (6) with respect to temperature at constant pressure yields

$$\frac{3\epsilon}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\ln\epsilon}{\partial T}\right)_P=-\gamma+\gamma\left(\frac{\partial\ln\alpha}{\partial\ln V}\right)_T+\left(\frac{\partial\ln\alpha}{\partial T}\right)_V, \tag{7}$$

where $\gamma=(\partial\ln V/\partial T)_P$ is the volume thermal expansion. The right-hand side of Eq. (7) consists of three contributions. The first, $-\gamma$, represents the change in ϵ due to change in density. The second, $\gamma(\partial\ln\alpha/\partial\ln V)_T$, is the change in ϵ due to the change in the polarizability of a fixed number of particles with changing volume. These two contributions together constitute the total effect due to volume expansion and are referred to as the pure volume effect. The third contribution, $(\partial\ln\alpha/\partial T)_V$, is the volume-independent or pure temperature effect.

In Eq. (7), the left-hand side and γ are determined from direct measurements. There are two unknowns: $(\partial\ln\alpha/\partial\ln V)_T$ and $(\partial\ln\alpha/\partial T)_V$. The first of these can be determined from the pressure dependence of ϵ as follows. The logarithmic pressure derivative of Eq. (6) at constant temperature yields[4]

$$\frac{3\epsilon}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\ln\epsilon}{\partial P}\right)_T=-\beta\left(\frac{\partial\ln\alpha}{\partial\ln V}\right)_T+\beta, \tag{8}$$

where $\beta=-(\partial\ln V/\partial P)_T$ is the volume compressibility. All the quantities in Eqs. (7) and (8) are thus known except $(\partial\ln\alpha/\partial T)_V$, which is then determined by substitution.

The various quantities in Eqs. (7) and (8) are given in Table IV for the three thallous halides. These quantities are evaluated at 20°C and 1 bar because the values of γ and β used in calculating the various coefficients are most accurately known at these conditions. The results show that the two volume-dependent contributions, $-\gamma$ and $\gamma(\partial\ln\alpha/\partial\ln V)_T$, have opposite signs, but their sum, i.e., the total volume-dependent effect is positive for the three halides. The pure temperature contribution $(\partial\ln\alpha/\partial T)_V$, on the other hand, is negative and determines the sign of $(\partial\ln\epsilon/\partial T)_P$ in all cases.

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[11] W. Lehfeldt, Z. Physik **85**, 717 (1933).

[12] Since results from different samples agreed well and also agreed with literature values from various sources (Refs. 2–4), we do not believe impurities play an important role in the temperature range (80–300°K) of interest.

[13] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1949), Appendix 3, p. 169.

TABLE IV. The various contributions to the temperature dependence of the dielectric constant of the thallous halides as defined by Eq. (7). Various quantities appearing in Eqs. (7) and (8) are also listed. All quantities are evaluated at 293°K.

Compound	ϵ	$K^*\left(\frac{\partial \ln\epsilon}{\partial P}\right)_T \times 10^3$ (kbar)$^{-1}$	$\beta\times10^3$ (kbar)$^{-1}$	$K^*\left(\frac{\partial \ln\epsilon}{\partial T}\right)_P \times 10^4$ [a] (°K)$^{-1}$	$-\gamma\times10^4$ (°K)$^{-1}$	$\gamma\left(\frac{\partial \ln\alpha}{\partial \ln V}\right)_T \times 10^4$ (°K)$^{-1}$	$\left(\frac{\partial \ln\alpha}{\partial T}\right)_V \times 10^4$ (°K)$^{-1}$
TlCl	32.2	−1.64	4.33	−0.357	−1.603	2.210	−0.964
TlBr	30.0	−1.74	4.84	−0.362	−1.535	2.090	−0.917
TlI (ortho.)	21.2	−0.88	7.55	−0.092	−1.250	1.393	−0.235
TlI (cubic)	29.6	−1.44	5.84	−0.397	−1.528	1.910	−0.779

[a] Note: $K^*=3\epsilon/(\epsilon-1)(\epsilon+2)$.

Recently, Havinga and Bosman[4] demonstrated that the sign of $(\partial \ln\alpha/\partial T)_V$ is structure-sensitive, being positive for ionic crystals (alkali halides and MgO) having the NaCl structure, and negative for crystals having CsCl structure. For the alkali halides this contribution is small in absolute magnitude, and the sign of $(\partial \ln\epsilon/\partial T)_P$ is determined by total volume-dependent effect which is positive in all cases. In the case of TlI, the results in Table IV show that $(\partial \ln\alpha/\partial T)_V$ is negative for both phases; however, its value in the orthorhombic phase is less than one-third that in the cubic phase. This along with a smaller positive volume-dependent contribution account for the fact that $(\partial \ln\epsilon/\partial T)_P$ for this phase is about six times smaller than its value for the cubic phase (see Table II).

Although the dielectric constant of TlI increases by 35% at the orthorhombic-to-cubic transition, it is easily shown, from Eq. (6) and the fact that the volume decreases by 3.4% at the transition,[1] that the total polarizability per molecule is independent of structure. Thus the change in ϵ at the transition can be completely accounted for by the change in density.

C. Optical and Infrared Polarizability

The total macroscopic polarizability α can be separated into two components

$$\alpha=\alpha_{\mathrm{op}}+\alpha_{\mathrm{ir}}. \tag{9}$$

The optical, or high-frequency, contribution arises from the displacements of the electronic charge distributions of the ions relative to the nuclei. The infrared contribution arises from the combined effects of the displacement of the ions and the resulting displacements of the electronic charge distributions. α_{op} is related to the high-frequency dielectric constant n^2 (n = refractive index) by a relation similar to Eq. (6) with ϵ replaced by n^2 and α by α_{op}. From Eq. (9) we get

$$\left(\frac{\partial \ln\alpha}{\partial \ln V}\right)_T=\frac{\alpha_{\mathrm{op}}}{\alpha}\left(\frac{\partial \ln\alpha_{\mathrm{op}}}{\partial \ln V}\right)_T+\frac{\alpha_{\mathrm{ir}}}{\alpha}\left(\frac{\partial \ln\alpha_{\mathrm{ir}}}{\partial \ln V}\right)_T, \tag{10}$$

$$\left(\frac{\partial \ln\alpha}{\partial T}\right)_V=\frac{\alpha_{\mathrm{op}}}{\alpha}\left(\frac{\partial \ln\alpha_{\mathrm{op}}}{\partial T}\right)_V+\frac{\alpha_{\mathrm{ir}}}{\alpha}\left(\frac{\partial \ln\alpha_{\mathrm{ir}}}{\partial T}\right)_V. \tag{11}$$

In order to evaluate the various contributions in Eqs. (10) and (11), the temperature and pressure dependence of the refractive index are needed. Unfortunately, there appear to be no such data for the thallous halides. However, the temperature dependence of the refractive index of a mixed crystal containing 45.7 mole% TlBr and 54.3 mole% TlI (better known as KRS-5) has been reported.[14] This crystal has the cubic CsCl structure and its static and optical dielectric constants and other physical properties are not much different than those of TlBr. Thus the reported results on KRS-5 can be used to estimate the relative importance of the optical and infrared terms in Eqs. (10) and (11) for the thallous halides.

The magnitudes of the optical and infrared terms in Eqs. (10) and (11) are now estimated for TlBr. It is assumed that $(dn/dT)_P$ for TlBr is comparable to that for KRS-5, namely $(dn/dT)\approx-2\times10^{-4}/°\mathrm{K}$ at 20°C and 1 bar.[14] If it is further assumed that the change in n with temperature and pressure is mostly due to the change in volume (i.e. $(\partial \ln\alpha_{\mathrm{op}}/\partial T)_V\approx0$),[15] one gets $(dn/dP)\approx6.3\times10^{-3}/\mathrm{kbar}$ at 20°C and 1 bar. From these slopes and the value of n ($=2.32$) we obtain $(\partial \ln\alpha_{\mathrm{op}}/\partial \ln V)_T=0.44$. The ratios $\alpha_{\mathrm{op}}/\alpha$ and $\alpha_{\mathrm{ir}}/\alpha$ can be calculated from the values of ϵ and n and Eqs. (6) and (9). At 20°C and 1 bar the values are $\alpha_{\mathrm{op}}/\alpha=0.66$ and $\alpha_{\mathrm{ir}}/\alpha=0.34$. Substituting these results into Eqs. (10) and (11) yields $(\partial \ln\alpha_{\mathrm{ir}}/\partial \ln V)_T=3.15$ and $(\partial \ln\alpha_{\mathrm{ir}}/\partial T)_V=-2.7\times10^{-4}/°\mathrm{K}$.

From the above considerations on TlBr, we conclude that for the thallous halides the predominant contributions to the two terms $(\partial \ln\alpha/\partial \ln V)_T$ and $(\partial \ln\alpha/\partial T)_V$ arise from the infrared polarizability. The contributions from the optical polarizability are much smaller.

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[14] W. S. Rodney and I. H. Malitson, J. Opt. Soc. Am. 46, 956 (1956).

[15] This assumption may not be strictly correct, but it should serve as a good approximation. The point we wish to make on the basis of this assumption is that in absolute value $(\partial \ln\alpha_{\mathrm{op}}/\partial T)_V \ll (\partial \ln\alpha_{\mathrm{ir}}/\partial T)_V$. This inequality has been demonstrated for as widely varying substances as alkali halides (Ref. 4) and SrTiO$_3$ [G. A. Samara, Phys. Rev. 151, 378 (1966)] and should hold for the thallous halides also. For example, for KCl $(\partial \ln\alpha_{\mathrm{op}}/\partial T)_V=-0.6\times10^{-5}/°\mathrm{K}$ and $(\partial \ln\alpha_{\mathrm{ir}}/\partial T)_V=10.8\times10^{-5}/°\mathrm{K}$; the corresponding values for SrTiO$_3$ are $-0.48\times10^{-5}/°\mathrm{K}$ and $-12.1\times10^{-5}/°\mathrm{K}$. Havinga and Bosman (Ref. 4) have shown on theoretical grounds that for various halides $(\partial \ln\alpha_{\mathrm{op}}/\partial T)_V$ is of the order of $-0.3\times10^{-5}/°\mathrm{K}$. In any case, one can easily show that any reasonable deviations from our assumption will not affect the main conclusions.

D. Pure Volume Contributions

As noted earlier the two volume-dependent contributions $-\gamma$ and $\gamma(\partial \ln\alpha/\partial \ln V)_T$ have opposite signs. The $-\gamma$ term is negative and its origin is clear. It is a density term which causes a decrease in ϵ with increasing temperature due to a decrease in the density of polarizable particles.

The $\gamma(\partial \ln\alpha/\partial \ln V)_T$ contribution, which on the basis of the discussion of the last section is due mostly to the infrared term, is positive. It is in absolute magnitude (see Table IV) the largest contribution to the temperature dependence of ϵ. The origin of $(\partial \ln\alpha_{\mathrm{ir}}/\partial \ln V)_T$ is generally discussed in terms of a classical ionic model consisting of point charges held apart by a repulsive potential of either the Born or Born-Mayer type. Such a model leads to an infrared polarizability inversely proportional to the restoring force. As the lattice expands, the restoring forces between ions decrease and therefore α_{ir} increases so that $(\partial \ln\alpha_{\mathrm{ir}}/\partial \ln V)_T$ is positive. Havinga and Bosman,[4] using such a model, calculated values of this quantity for a number of alkali halides and TlBr. Reasonable agreement with experimental values was obtained for either potential. For TlBr the calculated values of $(\partial \ln\alpha_{\mathrm{ir}}/\partial \ln V)_T$ are 4.0 and 3.8 using the Born and Born-Mayer potentials, respectively. As shown in the last section, the experimental value is ≈ 3.2 which is in fair agreement with the theoretical values.

Fuchs,[16] on the basis of this model and using a Born-Mayer potential, calculated values of $\gamma(\partial \ln\epsilon/\partial \ln V)_T$ for a number of halides. This quantity is easily shown to be related to $(\partial \ln\alpha/\partial \ln V)_T$ by

$$\gamma\left(\frac{\partial \ln\epsilon}{\partial \ln V}\right)_T=\frac{(\epsilon-1)(\epsilon+2)}{3\epsilon}\left[-\gamma+\gamma\left(\frac{\partial \ln\alpha}{\partial \ln V}\right)_T\right]. \qquad (12)$$

Fuchs compared the theoretical results with the then available experimental values for LiF, NaCl, and KCl. The theoretical values were about two thirds of the experimental ones. He attributed the discrepancy to the volume dependence of the effective ionic charge (or ionic overlap) which is neglected in the theory. The theoretical values were brought into better agreement with experimental values by including an overlap correction term computed on the basis of the shell model of Dick and Overhauser.[17]

From the present experimental results we calculate for $\gamma(\partial \ln\epsilon/\partial \ln V)_T$ values of $6.71\times10^{-4}/°\mathrm{K}$ and $5.73\times10^{-4}/°\mathrm{K}$ for TlCl and TlBr, respectively. The theoretical values calculated by Fuchs, without overlap correction, are $7.25\times10^{-4}/°\mathrm{K}$ and $7.74\times10^{-4}/°\mathrm{K}$, respectively. Thus, for the thallous halides the disagreement between theory and experiment is in the direction opposite to that for the alkali halides. Including an overlap correction term would make the disagreement worse. However, as we shall see later, the influence of ionic overlap, as measured by the value of the effective charge, is less for the thallous halides than it is for the alkali halides.

E. Pure Temperature Effect

The pure temperature contribution $(\partial \ln\alpha/\partial T)_V$ is negative and determines the sign of $(\partial \ln\epsilon/\partial T)_P$ in the thallous halides. The origin of this effect is generally discussed using a model of an ion in a potential well.[18] For a parabolic well the force constant k is independent of amplitude, and the polarizability, which is proportional to $1/k$, is thus independent of temperature. Any deviation from a parabolic potential causes k, and hence α, to be amplitude- or temperature-dependent.

A detailed theoretical treatment of the anharmonic contributions to the dielectric constant of ionic crystals has been given by Szigeti.[19] He treated together the effects of anharmonic terms in the potential energy and nonlinear terms in the dipole moment. The latter arise from the deformation of the electron shells during the course of lattice vibrations. Szigeti showed that if the potential energy and dipole moment are represented as power series in the displacements, then the lattice (or infrared) contribution to the dielectric constant, i.e., $\epsilon-\epsilon_{\mathrm{op}}$, is given by

$$\epsilon-\epsilon_{\mathrm{op}}=[4\pi N(Ze^*)^2/\bar{M}\omega_0^2][(\epsilon_{\mathrm{op}}+2)/3]^2+G=\eta+G. \qquad (13)$$

The first term on the right-hand side (denoted by η) represents the lattice contribution to the dielectric constant in the absence of anharmonic effects. N is the density of anion-cation pairs, and $\bar{M}$ is their reduced mass. Ze^* is the effective ionic charge, and ω_0 is the infrared absorption frequency. The second term G represents the anharmonic contribution. It is obtained as a power series in $(\bar{n}_i+\frac{1}{2})\hbar/\omega_i$ where $\bar{n}_i$ is the mean value of the quantum number of the ith lattice wave of frequency ω_i and is given by

$$\bar{n}_i=(e^{\hbar\omega_i/kT}-1)^{-1}. \qquad (14)$$

The sign of the term $(\partial \ln\alpha/\partial T)_V$, which is proportional to G, has been recently discussed[4,16] in terms of the different contributions to G. It is found that G consists of two terms. The first is a negative contribution arising from fourth-order potential and third-order nonlinear dipole moment terms. The second contribution is positive and arises from third-order potential and second-order terms in the dipole moment which result from the interaction of acoustical and optical modes. Havinga and Bosman found that this contribution is

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[16] R. Fuchs, Technical Report No. 167, Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Mass., 1961 (unpublished).

[17] B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

[18] F. C. Frank, Trans. Faraday Soc. **42**, 250 (1946).

[19] B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949); Proc. Roy. Soc. (London) **A204**, 51 (1950); **A252**, 217 (1959); **A261**, 274 (1961).

TABLE V. Calculated values of the harmonic and anharmonic lattice contributions to the dielectric constant and the effective charge of TlCl and TlBr. Values of the static and optical dielectric constants and the infrared absorption frequencies are also given. The corresponding quantities for four alkali halides are given for comparison.

Compound	Structure	ϵ	$\epsilon\mathrm{r}_{\mathrm{p}}$[a]	$\dfrac{\eta}{\epsilon-\epsilon_{\mathrm{op}}}$	$\dfrac{G}{\epsilon-\epsilon_{\mathrm{op}}}$	$10^{-13}\omega_0$[b] $(\mathrm{sec})^{-1}$	$\dfrac{e^*}{e}$
TlCl	CsCl	32.2	5.1	1.371	−0.371	1.19	0.96
TlBr	CsCl	30.0	5.4	1.338	−0.338	0.90	0.95
NaCl	NaCl	5.6	2.3	0.969	0.031	3.09	0.73
KCl	NaCl	4.7	2.2	0.950	0.050	2.71	0.77
CsCl	CsCl	7.2	2.6	1.047	−0.047	1.87	0.89
CsBr	CsCl	6.5	2.8	1.041	−0.041	1.39	0.81

[a] Taken from N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, England, 1950), p. 12.
[b] Taken from Refs. 22 and 23.

structure-sensitive[20] and increases as the number of nearest neighbors decreases, thus offering an explanation for the change in the sign of $(\partial \ln\alpha/\partial T)_V$ of the alkali halides from negative to positive in going from the CsCl to the NaCl structure. The present data on TlI are in qualitative agreement with this result. $(\partial \ln\alpha/\partial T)_V$ becomes more negative as the substance transforms from the orthorhombic phase where each atom has seven nearest neighbors to the cubic phase where the number of nearest neighbors is eight. The fact that $(\partial \ln\alpha/\partial T)_V$ is strongly negative for the three thallous halides (cubic phase) implies that G is predominantly determined by the contribution arising from fourth-order potential and third-order dipole moment. As in the case of the alkali halides,[21] the influence of the third-order dipole moment is probably small compared with that of the fourth-order potential.

F. Magnitude of the Anharmonic Contribution G

From the present experimental results, it is possible to arrive at an estimate of the anharmonic contribution G for the thallous halides at room temperature. Szigeti[19] has shown that for temperatures above the Debye temperature Θ_D Eq. (14) reduces to $\bar{n}_i=[(kT/\hbar\omega_i)-\frac{1}{2}]$ and G can be written as

$$G=AT, \tag{15}$$

where A is assumed to be a constant independent of V and T. From Eqs. (13) and (15) we have

$$\left[\frac{\partial(\epsilon-\epsilon_{\mathrm{op}})}{\partial T}\right]_V=\left(\frac{\partial\eta}{\partial T}\right)_V+\left(\frac{\partial G}{\partial T}\right)_V=\left(\frac{\partial G}{\partial T}\right)_V=A, \tag{16}$$

where $(\partial\eta/\partial T)_V$ has been set $=0$ because all the quantities appearing in this term are considered unique functions of volume.[19] Therefore, from Eqs. (15) and (16) we get

$$G=T[\partial(\epsilon-\epsilon_{\mathrm{op}})/\partial T]_V. \tag{17}$$

Now the quantity in the square brackets in Eq. (17) can be written as

$$[\partial(\epsilon-\epsilon_{\mathrm{op}})/\partial T]_V\approx(\partial\epsilon/\partial T)_V$$
$$=(\partial\epsilon/\partial T)_P+(\gamma/\beta)(\partial\epsilon/\partial P)_T. \tag{18}$$

This follows from the assumption that ϵ_{op} is a unique function of volume. The derivatives of ϵ can then be evaluated directly from our experimental results. $(\partial\epsilon/\partial T)_V$ can also be written in terms of the total polarizability. From Eq. (6) it is easily shown that

$$(\partial\epsilon/\partial T)_V=\tfrac{1}{3}[(\epsilon-1)(\epsilon+2)](\partial \ln\alpha/\partial T)_V; \tag{19}$$

$(\partial\epsilon/\partial T)_V$, and therefore G, is then evaluated from the results in Table IV.

In Table V we list values of ϵ and ϵ_{op} and the calculated quantities $G/(\epsilon-\epsilon_{\mathrm{op}})$ and $\eta/(\epsilon-\epsilon_{\mathrm{op}})$ for TlCl and TlBr (ϵ_{op} is not known well enough for TlI). As can be seen from Eq. (13), the latter two quantities represent the fraction of the lattice contribution to the dielectric constant due to anharmonic and harmonic effects, respectively. All the quantities in Table V are evaluated at 293°K, a temperature much higher than the Debye temperatures (e.g., $\Theta_D\approx 120$°K for both TlCl and TlBr), so that the high-temperature approximation is valid. For comparison purposes, we also give in Table V the appropriate quantities for four alkali halides. These were calculated from the data of Havinga and Bosman.[4]

As can be seen from the results, anharmonic effects account for about 30–40% of the lattice contribution to the dielectric constant of the thallous halides as compared with less than 5% in the case of the alkali halides. An interesting feature of the results is that for the thallous halides and those alkali halides having the CsCl structure, the anharmonicities act to reduce the effect of the harmonic contribution η. On the other hand, for alkali halides having the NaCl structure, the anharmonicities enhance the harmonic contribution.

G. Calculation of the Effective Charge e^*

From the above calculated values of the harmonic contribution η and the infrared absorption frequencies

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[20] Havinga and Bosman (Ref. 4) neglect nonlinear terms in the dipole moment and consider only anharmonic potential terms.

[21] V. V. Mitskevich, Fiz. Tverd. Tela 3, 3036 (1961) [English transl.: Soviet Phys.—Solid State 3, 2211 (1962)].

ω_0 reported by Jones *et al.*,[22] it is possible to calculate the values of the effective charge e^*. From Eq. (13) we see that

$$\eta=[4\pi N(Ze^*)^2/\bar{M}\omega_0^2][(\epsilon_{\text{op}}+2)/3]^2, \qquad (20)$$

where Z is the valence ($Z=1$ for the thallous halides). All quantities in Eq. (20) are known except e^*. The calculated values of e^* for TlCl and TlBr as well as those for the four alkali halides mentioned earlier are given in Table V. The results are reported as e^*/e, i.e., the ratio of the effective charge to the electronic charge e.

In the ideal case of deformable ions which do not overlap, the ratio e^*/e is unity. In real crystals, however, the ions overlap to some extent, and the concept of an effective charge was introduced into the theory to account for polarization effects associated with this overlap.[17,19] Deviations of e^*/e from unity arise from two effects: (1) Short-range repulsive interactions between the electron clouds of adjacent ions which modify the electronic dipole moments, and (2) redistribution of charge and overlap when the ions move in the course of lattice vibrations. It is rather interesting to note from the results that e^*/e is much closer to unity for the thallous halides than it is for the alkali halides. The reason for the difference in e^*/e between the thallous and alkali halides must be related to the fact that the outermost electrons of the thallous ion exist in spherically symmetric *s* orbitals, whereas those of the alkali metal ions (except Li) are in highly directional *p* orbitals. Intuitively, one suspects that the above two effects causing the deviation of e^*/e from unity may be more pronounced in the case of the *p* orbitals. Clearly, no independent determination of e^* is possible on completely classical grounds, and the solution requires quantum mechanical treatment. Dick and Overhauser[17] treated the case of the alkali halides semiclassically.

It is interesting to compare the values of e^*/e for the thallous halides in Table V with those calculated by neglecting anharmonic contributions to the dielectric constant, i.e., by setting $\epsilon-\epsilon_{\text{op}}=\eta$ in Eq. (13). The results are $e^*/e=0.82$ for both TlCl and TlBr. Szigeti,[19] using the early value of $\omega_0=1.61\times10^{13}$ sec^{-1} given by Barnes,[23] calculated $e^*/e=1.08$ for TlCl. According to Jones *et al.*,[22] the value of ω_0 given by Barnes is in error, and the correct value is 1.19×10^{13} sec^{-1}. This is the value used in our calculations, and it removes the difficulty of having $(e^*/e)>1$. It may be pointed out in passing that this new value of ω_0 for TlCl yields a value of 1.04 for the ratio of the calculated to the observed compressibility (i.e., $\beta_{\text{calc}}/\beta_{\text{obs}}$) in Szigeti's theory.[24] Barnes's value of ω_0 yields a ratio of 0.57.

H. Curie-Weiss Behavior of the Dielectric Constant

As can be seen from Fig. 1, the temperature dependence of ϵ of TlCl and TlBr below about 225°K obeys the Curie-Weiss law

$$\epsilon=c/(T-T_0). \qquad (21)$$

The recent results of Rao and Smakula[3] and Lowndes[2] indicate that this behavior holds down to 1.5°K. At 1 bar, $T_0=-1650$°K and -1820°K and $c=6.2\times10^4$°K and 6.3×10^4°K for TlCl and TlBr, respectively. These results allow one to calculate ϵ at very low temperatures.

The Curie-Weiss behavior of ϵ is generally associated with the temperature dependence of ϵ of ferroelectrics (or antiferroelectrics) above their Curie points (i.e., in the paraelectric state), and it foreshadows a transition to a ferroelectric phase. It should be noted, however, that Curie-Weiss behavior has been recently observed at low temperatures in alkali halides containing small concentrations ($\approx10^{18}$ cm^{-3}) of polar impurities such as OH$^-$, CN$^-$, and Li$^+$.[25] This behavior and the value of ϵ are found to be strongly dependent on impurity concentration. Because present results from different samples agreed well and also agreed with reported results from various sources,[2–4] we do not believe that such impurity effects are responsible for the Curie-Weiss behavior of the thallous halides. It is very unlikely that all the different samples had the same concentration and type of impurity. In addition measurements down to 1.5°K on TlCl and TlBr [2,3] showed none of the anomalies in ϵ usually associated with polar impurities.[25]

The question of the existence of ferroelectric behavior in diatomic ionic crystals has received considerable attention. In a theory which associates the onset of ferroelectric behavior in a substance with the vanishing of a transverse optic mode of long wavelength (a so-called "soft" mode), Cochran[26] has pointed out that there is no reason in principle why a diatomic crystal should not have a ferroelectric phase. Recent studies of the phonon dispersion relations of some diatomic semiconductors (e.g., SnTe, PbTe) have exhibited such a soft mode and thus suggested the possible existence of ferroelectric behavior.[27] Direct measurements of ϵ are prevented by the high conductivities of these semiconductors. In view of the relatively high dielectric constants (compared with most normal dielectrics) and their Curie-Weiss behavior in TlCl and TlBr, it is of interest to inquire into the possibility of a connection between the results and the theory.

Of prime importance in the theory is the Lyddane-Sachs-Teller relation which relates the frequencies of the transverse and longitudinal optic modes (at $k\approx0$) in a diatomic cubic crystal to the static and high-frequency

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[22] G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261**, 10 (1961).

[23] R. B. Barnes, Z. Physik **75**, 723 (1932).

[24] In this calculation we use the more recent value of 4.25×10^{-6}(kg/cm^2)$^{-1}$ for β_{obs}. Szigeti used a value of 4.8×10^{-6} in his original calculation.

[25] See for e.g., W. Känzig, H. R. Hart, Jr., and S. Roberts, Phys. Rev. Letters **13**, 543 (1964).

[26] W. Cochran, Advan. Phys. **9**, 387 (1960).

[27] G. S. Pawley, W. Cochran, R. A. Cowley, and G. Dolling, Phys. Rev. Letters **17**, 753 (1966).

dielectric constants. The relation is

$$\omega_L^2/\omega_T^2=\epsilon/\epsilon_{\mathrm{op}}. \tag{22}$$

According to the theory

$$\omega_T^2 \propto 1/\epsilon \propto (T-T_0), \tag{23}$$

so that ω_T should decrease with decreasing temperature and vanish at T_0. Sufficiently detailed data on the effects of temperature on ω_T of TlCl and TlBr are not available. Jones *et al.*[22] measured ω_T of both compounds at 300 and 4°K, but, unfortunately, their results do not even establish a trend for the temperature dependence of ω_T. It is found that ω_T of TlBr decreases from 0.9 to 0.89×10^{13} sec^{-1} while that of TlCl increases from 1.19 to 1.24×10^{13} sec^{-1} between 300 and 4°K. It is somewhat surprising that the two compounds behave differently.

In Eq. (23) the effects of changes in ω_L and ϵ_{op} which appear in Eq. (22) have been neglected. In the absence of experimental results, it is difficult to assess accurately the effects of these changes. If in Eq. (22) ω_L is assumed to be independent of temperature then

$$-2(\partial \ln\omega_T/\partial T)_P=(\partial \ln\epsilon/\partial T)_P-(\partial \ln\epsilon_{\mathrm{op}}/\partial T)_P. \tag{24}$$

From the measured value of $(\partial \ln\epsilon/\partial T)_P$ and the value of $(\partial \ln\epsilon_{\mathrm{op}}/\partial T)_P$ calculated by assuming that $(dn/dT)_P$ for TlBr is the same as that for KRS-5, we obtain for TlBr at 1 bar and 20°C $(\partial \ln\omega_T/\partial T)_P\approx 1\times10^{-4}/°\mathrm{K}$. This is a fairly small change which may be difficult to measure accurately.[28]

V. SUMMARY

(1) The static dielectric constants of TlCl, TlBr, and TlI (both phases) decrease with increasing pressure. At the orthorhombic → cubic transformation in TlI (at 4.8 kbar and 25°C) the dielectric constant increases 35%. This increase is entirely due to the decrease in volume, the total polarizability per molecule being independent of crystal structure.

(2) At high temperatures the dielectric constant and dielectric loss are predominantly determined by the formation and transport of lattice defects and increase exponentially with increasing temperature. The activation energies calculated from the dielectric loss measurements in this region are 0.84 eV for TlCl and 0.85 eV for TlBr. These are in good agreement with values obtained from ionic-conductivity measurements.

(3) At low temperatures the dielectric constants of the three compounds decrease with increasing temperature. The temperature dependence of the dielectric constant at constant pressure is separated into volume-dependent and volume-independent contributions. For the thallous halides the latter contribution, which is determined entirely by anharmonic effects, is large and determines the sign of $(\partial\epsilon/\partial T)_P$.

(4) The results are discussed in terms of Szigeti's theory under the assumption that the optical dielectric constant ϵ_{op} is a unique function of volume. It is found that at 20°C anharmonic effects account for 30–40% of the lattice contribution to the static dielectric constant. Their contribution is negative and acts to reduce the effect of the harmonic term. It is also found that the ratio of the effective ionic charge to the electronic charge, e^*/e, is 0.96 for TlCl and 0.95 for TlBr. These are to be compared with a value of 0.82 for both compounds calculated without taking account of anharmonic effects.

(5) At low temperatures the dielectric constants of TlCl and TlBr obey a Curie-Weiss law. This behavior is generally associated with the temperature dependence of the dielectric constant of ferro- and antiferroelectrics above their Curie points.

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[28] *Note added in proof.* After the submission of this work, a paper by E. R. Cowley and A. Okazaki on the lattice dynamics of TlBr appeared in the literature [Proc. Roy. Soc. (London) **A300**, 45 (1967); also private communication from E. R. Cowley]. They measured the frequencies of the normal modes at 100 and 295°K using inelastic neutron scattering. From their data (for $k=0$) we calculate $(\partial \ln\omega_T/\partial T)_P\approx 0.74\times10^{-4}/°\mathrm{K}$ and $(\partial \ln\omega_L/\partial T)_P\approx -0.60\times10^{-4}/°\mathrm{K}$, which are indeed small changes. On the basis of their results the authors also conclude that there is a large intrinsic anharmonic contribution to the dielectric constant in TlBr, and that it is the temperature dependence of the polarizability rather than of the TO frequency (at zero applied frequency) which leads to the sign of the temperature dependence of ϵ. These conclusions are in agreement with ours.