If we assume that f_0 is the Maxwell-Boltzmann distribution function and that τ_0 varies inversely as the first power of the velocity, corresponding to a constant mean free path, the foregoing constants have the following values

$$\sigma_0 = ne\mu, \tag{22a}$$

$$\alpha = -ne(3\pi\mu^2)/(8c), \tag{22b}$$

$$I = ne(9\pi\mu^3)/(16c^2), \tag{22c}$$

where μ, the mobility, is

$$\mu = (8e\lambda)/(3\pi m\bar{V}) \tag{23}$$

in which λ is the mean free path and

$$\bar{V} = 4(kT/2\pi m)^{\frac{1}{2}}. \tag{24}$$

The coefficients ϵ', λ', and η' in (3) can readily be expressed in terms of integrals of the type (13). In the isotropic approximation these reduce to

$$\epsilon' = \lambda' = \eta' = -(9\pi\mu^2\alpha)/(8c^2)$$

in which α is given by (22b).

The writer is indebted to Professor Estermann (see accompanying paper) and to members of the Bell Telephone Laboratories, in particular Drs. Shockley, Pearson, and Suhl, for discussions of the topic presented here. These investigators have carried out extensive experimental and theoretical work bearing on this subject which will be published[6] in the near future.

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[6] See, for example, W. Shockley, Phys. Rev. 78, 172 (1950).

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Effect of Pressure on the Low Frequency Dielectric Constant of Ionic Crystals*

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Data on the pressure dependence of the dielectric constant ϵ of MgO, LiF, NaCl, KCl and KBr at 1000 c.p s. and room temperature are given as a function of hydrostatic pressure from 0 to 8000 bars. The dielectric constants are found to decrease with an initial slope $(\partial \ln\epsilon/\partial p)_T$ ranging from -0.32×10^{-5} bar^{-1} in the case of MgO to -1.17×10^{-5} bar^{-1} in the case of KBr. Present lattice theories are only capable of explaining these data if the inner field decreases with increasing pressure.

I. INTRODUCTION

MANY measurements have been made on the effect of hydrostatic pressures on the dielectric constant of gases and liquids, and these are reviewed in a recent article by Bridgman.[1] Previous measurements on solids have been concerned primarily with the effect of pressure on the Curie temperature of rochelle salt,[2] and of barium titanate.[3] This report presents data on a very simple class of solid dielectrics, ionic crystals, for which there is sufficient knowledge to allow a prediction concerning the pressure dependence of the low frequency dielectric constant. To the extent that this prediction is verifiable by experiment, the validity of present lattice theories can be tested.

There are large changes in the densities of gases and liquids at high pressures, and the dielectric constant is found to increase, as might be expected from the fact that the number of dipoles per unit volume increases. The density changes in ionic crystals are comparatively small, at most about 5 percent for pressures up to 10,000 bars. The dielectric properties of these solids could be influenced more by the changes in polarizabilities and inner fields under high pressures than by the changes in density. In fact, Mueller[4] has calculated the effect of pressure on the optical dielectric constant of some ionic crystals from strain optical data,[5] and, assuming the Lorentz form for the inner field, has shown that the polarizabilities of the ions decrease with increasing pressure. He finds the relative change of the

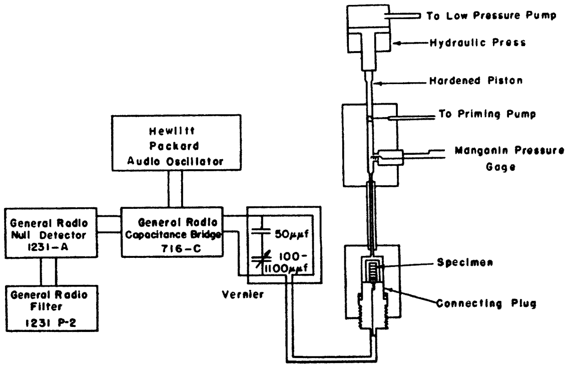

FIG. 1. Experimental set-up. Schematic diagram of high pressure system and electrical apparatus.

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* The experiment was carried out in the High Pressure Laboratory of the Institute for the Study of Metals and was supported in part by funds made available under contract N-6ori-20-XX between the ONR and the University of Chicago.

[1] P. W. Bridgman, Rev. Mod. Phys. 18, 69 (1946).

[2] D. Bancroft, Phys. Rev. 53, 587 (1938).

[3] W. J. Merz, Phys. Rev. 78, 341 (1950).

[4] H. Mueller, Phys. Rev. 47, 947 (1935).

[5] F. Pockels, *Lehrbuch der Kristalloptik* (Teuber, Leipzig, 1906), p. 480.

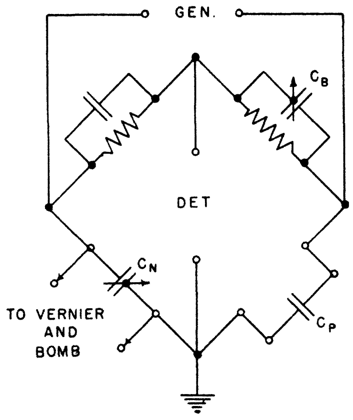

FIG. 2. Schering bridge used in substitution method. Condenser C_N measures the unknown capacity and condenser C_B compensates for changes in the resistance of the unknown.

polarizability to be about one-half the relative change in density. Thus, for the polarizability of the electrons of the ions, which seemingly should be rather insensitive to pressure, the relative changes with increasing pressure are of the same order of magnitude as are the relative changes in density.

At optical frequencies the dielectric constant arises wholly from the polarizabilities of the ions, but at frequencies lower than the characteristic frequency of the lattice, there is also a polarization caused by the displacement of the lattice of positive ions with respect to the lattice of negative ions. Bretscher[6] has found that the change in dielectric constant with temperature is largely caused by the change in the polarizability of the lattice, and he suggests that the change in lattice polarization also plays an important role in the change in the dielectric constant with pressure. The lattice polarization may reasonably be expected to change markedly with pressure, because its magnitude is large or small depending on whether the restoring force for the displacement is weak or strong. Since the effect of pressure is usually to increase these restoring forces, an increase in pressure should reduce the lattice polarization. If the relative change in the lattice polarization is large compared to the relative change in density, the low frequency dielectric constant should decrease. The research described below was undertaken to ascertain whether the low frequency dielectric constant of ionic crystals does indeed decrease at high pressures.

II. EXPERIMENTAL METHOD

(A) Electrical Measurements

Since the low frequency dielectric constant of ionic crystals is relatively constant through the low frequency range into the infra-red, measurements are made only at 1000 c.p.s. The change in the dielectric constant with pressure is determined by measuring the change of capacity of a parallel plate condenser with a capacitance bridge and auxiliary apparatus, shown schematically in Fig. 1. The measurements of capacity are made by a substitution method in the manner illustrated by Fig. 2. In order to measure changes of capacity as small as 0.01 $\mu\mu$f, a capacity vernier was constructed from a small fixed condenser in series with a large variable condenser. The vernier is shown in Fig. 1.

The bridge condenser is used as the capacity standard for these measurements. It was checked against another condenser of the same model and found to be within the manufacturer's specification, which states that measurements of small capacities by substitution methods have an error of $\pm 0.1\ \mu\mu$f. The variable condenser in the vernier was calibrated against the bridge condenser. The capacity range of the bridge condenser used for this calibration is 3.0 $\mu\mu$f. There is very little scatter, even though the points are taken at the smallest intervals possible (every 0.2 $\mu\mu$f) on the scale of the bridge condenser. Since the scatter of the calibration points is small, the error in the capacities measured by the variable vernier condenser is at most the error of 3.0 $\mu\mu$f of the bridge condenser which is $\pm 0.1\ \mu\mu$f or ± 3 percent.

Capacity changes observed on the vernier condenser must be corrected for changes in the dissipation factor of the sample in order to obtain the true capacity change of the sample when it is exposed to the high pressure. This correction was found to be negligible for all the measurements reported here.

Connections are made with cable which has a capacitance of 13.5 $\mu\mu$f per foot and a temperature coefficient which is less than $2\times10^{-4}/^{\circ}\mathrm{C}$. It is estimated, taking into account the temperature coefficients of other parts of the system and the magnitudes of the capacities involved, that a fluctuation in ambient tem-

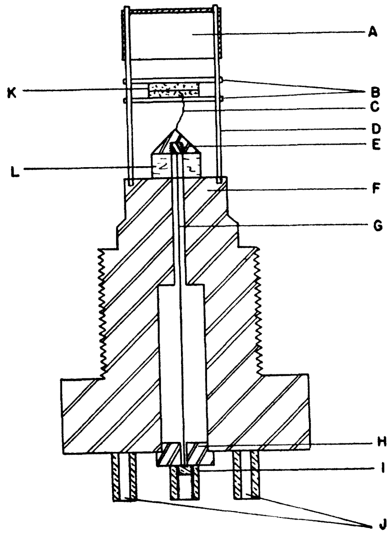

FIG. 3. Sample holder and plug for high pressure bomb. A. Pill box container for sodium. B. Sample supports and electrical grounds. C. 3 mil manganin wire. D. Supporting pins. E. Hardened steel cone with optical flat base and threaded hole. F. Hardened steel plug with top surface optically flat. G. 8-mil piano wire. H. Insulating bushing. I. High electrode. Threaded tube with threaded anchor soldered to piano wire. J. Ground electrodes. K. Slabs of dielectric. L. Sapphire washer with both faces optically flat.

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[6] E. Bretscher, Trans. Faraday Soc. **30**, 684 (1934).

TABLE I. Experimental data to be used in calculations.

	D.c. dielectric constant[a]	Optical dielectric constant[a]	Lattice constant[a]	Volume changes under high pressure at room temperature[b] $\frac{-\Delta V}{V_i}=ap-bp^2$		Thermal expansion[d]	Change of d.c. dielectric constant with temperature[d]	Change of refractive index with density[e]
	ϵ	ϵ_0	L (A)	a $\times 10^7$ bars	b $\times 10^{12}$ (bars)^2	$\left(\frac{\partial \ln V}{\partial T}\right)_p$ $\times 10^4$(°C)	$\left(\frac{\partial \ln\epsilon}{\partial T}\right)_p$ $\times 10^5$(°C)	$\frac{dn}{d \ln\rho}$
LiF	9.27	1.92	2.07	15.20	5.5	1.05	37.5	0.1
NaCl	5.62	2.25	2.81	43.1	49.6[c]	1.20	34.0	0.24
KCl	4.68	2.13	3.14	56.8	72.4[c]	0.96	30.3	0.23
KBr	4.78	2.33	3.29	67.0	105.3			0.35
MgO	9.8	2.95		5.95	1.0			

[a] Values for the first three columns were obtained from summaries of experimental values by K. Hojendahl, K. Danske Vidensk Selskab, **16**, No. 2 (1938).

[b] Volume changes under pressure were measured by Bridgman and Slater and are tabulated by F. Birch *et al.*, Geological Society of America, Special Papers No. 86, *Handbook of Physical Constants* (1942), p. 52.

[c] Values of a and b for NaCl and KCl are taken from the elastic constant measurements of D. Lazarus, Phys. Rev. **76**, 545 (1949).

[d] $(\partial \ln V/\partial T)_p$ and $(\partial \ln\epsilon/\partial T)_p$ are taken from a A. Eucken and A. Buchner, Zeits. f. physik. Chemie **B27**, 321 (1934).

[e] $dn/d \ln\rho$, is taken from E. Burstein and P. L. Smith, Phys. Rev. **74**, 229 (1948).

perature of 1°C will produce an error of 10^{-2} $\mu\mu$f. A pressure run lasts at most three hours. The temperature was always measured after a run and found to be within a half-degree of the temperature before the run. Therefore, the effects of room temperature fluctuations are insignificant.

(B) High Pressure Apparatus

The system for generating high pressures is similar to those previously described[7] and is shown schematically in Fig. 1. The pressure fluid is normal hexane. Pressures are measured by use of a manganin resistance gauge whose pressure coefficient of resistance $(\partial \ln R/\partial p)_T$ is 2.48×10^{-6} bar^{-1}, as determined by using the freezing point of mercury at 0°C.[8]

The main high pressure problem in this experiment was to make a packing for the electrical lead into the high pressure bomb. Most of the high pressure packings which are satisfactory for measuring resistances or for carrying currents into a high pressure chamber are unsatisfactory for our purpose, either because the capacity changes too much as a function of pressure, or because the capacity at zero pressure shifts after an application of high pressure. The type of electrical load which has proven most satisfactory for pressures up to 8000 bars is that shown in Fig. 3. The packing is similar to the type used extensively in the laboratory of Michels, but differs from it in that an Al_2O_3 crystal is used as the insulating washer instead of fused silica. The Al_2O_3 is less apt to fail under the high pressures, provided it is well annealed, and is polished to remove all sharp corners from which rupture may start. The washer is $\frac{5}{8}''$ in diameter, $\frac{1}{4}''$ thick and has a $\frac{1}{16}''$ diameter hole. The c-axis of the crystal is parallel to the axis of the hole so that the cylindrical geometry is preserved when pressure is applied. Both faces of the washer and all steel in contact with it are optically flat to $\frac{1}{4}$ of a wave-length of visible light, causing the surfaces to stick without the aid of adhesives. Nevertheless, a thin layer of a thermoplastic wax was used between the flat surfaces in order that a sudden release of pressure would not separate the washer from the steel parts and thus cause a leak.

In spite of all these precautions in the construction of the packing, long exposure to pressures higher than 8000 bars caused deterioration of the packing washer around the small hole in the washer. For this reason measurements on dielectric constants were restricted to pressures less than 8000 bars. The variation of the capacity of the electrical lead with sapphire packing is 0.15 $\mu\mu$f in 8000 bars, and its zero pressure capacity changes at most 0.01 $\mu\mu$f during a pressure cycle.

(C) Preparation of Samples

The samples are prepared in the form of parallel plate condensers by cleaving thin slabs from large

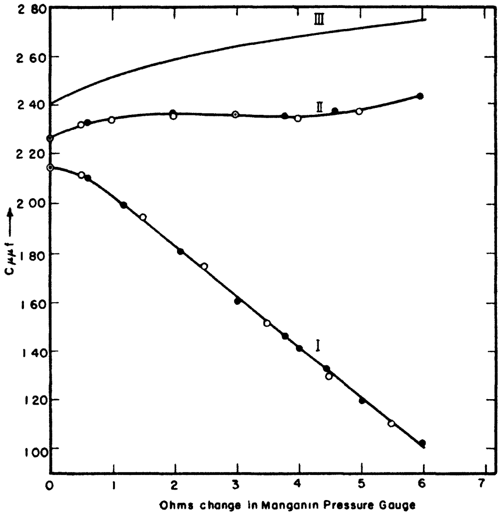

FIG. 4. Capacity measurements for a sample of NaCl. Curve *I* is change of capacity of plug and sample. Curve *II* is change of capacity of plug alone. Curve *III* is correction curve for the sample capacity required because the fringing capacity changes with pressure.

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[7] P. W. Bridgman, *Physics of High Pressures* (Macmillan Company, Inc., New York, 1931), Chapter 2.

[8] D. Lazarus, Phys. Rev. **76**, 547 (1949).

single crystals. The slabs are usually about 2 cm^2 in area and 1 mm thick. All the ionic crystals studied here are cubic and since the dielectric constant is the same in all directions in a cubic crystal, no attempt has been made to orient the crystals. It is likely, however, that the faces of the cleaved slabs are (100) planes, since these are the planes in the crystals which are most readily cleaved.

Platinum electrodes are sputtered onto the crystals in vacuum. This technique gives good adhesion to the crystal surface because the glow discharge, which accompanies the sputtering, cleans the crystal surface before the platinum deposits. Such surfaces were found to be superior to various silver and platinum paints and to evaporated aluminum, all of which deteriorated when exposed to the high pressure.

The actual geometry in which the condensers of the dielectric are used is shown in Fig. 3. Two slabs are held by brass plates which act both as supports and as electrical ground connections. The other connection is a 0.003″ insulated manganin wire, one end of which is soldered to the electrical lead at the top of the cone, while the other end is placed between the two slabs of the sample. The pill box at the top of the specimen holder contains sodium to keep the system dry.

(D) Measurements

The plug with the sample in place is mounted in the high pressure bomb, the bomb is filled with hexane and the capacity of the system is determined as a function of pressure. Next, the manganin lead wire is unsoldered, disconnecting the sample, and the procedure is repeated to ascertain the variation of the lead capacity with pressure. In order to find the variation in capacity of the sample itself, the second set of pressure measurements are subtracted from the first, and, since no guard rings are used on the samples, a correction is made for the fringing of the electric field around the edges of the slabs of dielectric.

The fringing capacity ΔC_f is determined experimentally since

$$\Delta C_f = \Delta M/(K_1 - 1),$$

where ΔM is the difference between the capacity of the sample when it is measured immersed in hexane and when it is measured immersed in air and K_1 is the dielectric constant of hexane at one atmosphere pressure. However, when a pressure run is made, the sample is always immersed in hexane and so the effective fringing capacity is $K\Delta C_f$ where K is the dielectric constant of hexane, which changes with pressure as measured by Chang.[9] Now, ΔC_f does not change appreciably with pressure since it depends on the geometry, which is relatively constant. Therefore, the effective fringing capacity varies with pressure as the dielectric constant of hexane.

Figure 4 shows a typical set of measurements for a sample of NaCl with a total initial capacity of 18.5 $\mu\mu$f. Curve *I* is the change of capacity of the lead and the sample; Curve *II* is the change of capacity of the lead alone, and Curve *III* is the change in the fringing capacity of the sample in the sample holder. Curve *III* is computed using the fact that for this sample $\Delta M = 0.77$ $\mu\mu$f. Note that in these curves the capacity origin is unimportant since the thing of interest is the change of capacity from its zero pressure value. The circles on Curves *I* and *II* represent readings taken with decreasing pressure, while the dots represent readings taken with increasing pressure. The circles serve as a check to determine whether the platinum electrode is worked off the surface of the crystal by the pressure cycle. To obtain the change in capacity ΔC of the sample, Curves *II* and *III* are subtracted from Curve *I*; and to give the relative change in capacity of the sample, ΔC is divided by the initial capacity C_i.

The relative change in dielectric constant $\Delta\epsilon/\epsilon_i$ follows directly from the relative change in capacity of the sample $\Delta C/C_i$, providing a correction is made for the effect of pressure on the geometry of the sample. This correction is easily made. Capacity is proportional to a length and the appropriate length here is the dimension of the crystal. Thus, $C \sim \epsilon l$ and $\Delta\epsilon/\epsilon_i = \Delta C/C_i - \Delta l/l_i$, neglecting second order terms. The quantity $\Delta l/l_i = \Delta V/(3V_i)$ is obtained from the volume measurements of Bridgman or others (Table I).

III. RESULTS

Figure 5 shows the results of the measurements for $\Delta\epsilon/\epsilon_i$. The origin of each curve is displaced in order to fit all curves of the same graph. For LiF and NaCl two sets of measurements on the same sample were made.

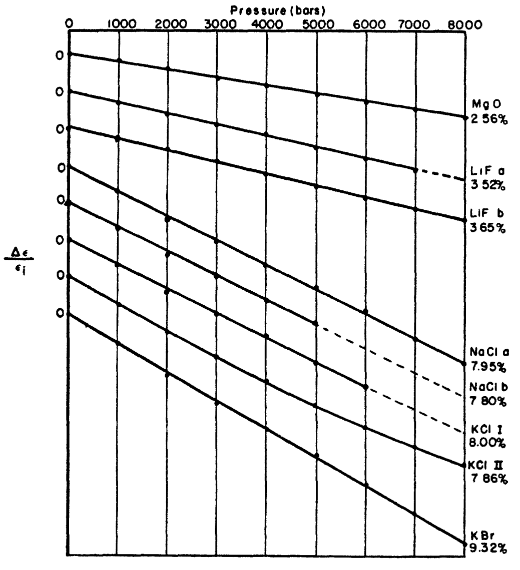

FIG. 5. The pressure dependence of the 1000 c.p.s. dielectric constant at room temperature. The origin of each curve is vertically displaced so that all curves fit on the same graph. The dashed line indicates an extrapolation. The total relative change is given at 8000 bars for all curves.

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[9] Z. T. Chang, Chin. J. Phys. 1 (No. 2), 1 (1934).

For KCl two measurements, each one on a different sample, were made. It is rather difficult to evaluate any spurious error associated with the high pressure problem. For this reason more than one run was made for several samples. The difference between two runs on the same sample gives a qualitative idea of the reproducilibity of the data.

The dielectric constant of all materials decreases with increasing pressure. For the hard materials LiF and MgO the dielectric constant is linear with pressure. For the softer materials, NaCl, KCl and KBr, there may be a slight tendency for the dielectric constant to decrease more slowly at the higher pressures. This tendency for most of the runs borders on the edge of the experimental error; but for KCl *II*, where the sample capacity is large enough so that its capacity change is very large compared to the corrections, the dielectric constant does decrease more slowly with increasing pressure.

The most significant quantity obtained from these measurements is the initial slope $(\partial \ln\epsilon/\partial p)_T$. The values of $-(\partial \ln\epsilon/\partial p)_T$ are listed in Table II. The error in each value is ±3 percent as a result of the estimated error in capacity measurements. The over-all error is listed with the average value of $-(\partial \ln\epsilon/\partial p)_T$. From these values of $(\partial \ln\epsilon/\partial p)_T$ it is possible to calculate the volume electrostrictive coefficient. The electrostriction is found to be so small that it can have no influence on the results of the measurements.

It may be of interest to see whether ϵ could be described as depending only on the volume and implicitly through it on the temperature and pressure. The validity of such an assumption would be tested by the extent to which we should have

$$\left(\frac{\partial \ln\epsilon}{\partial T}\right)_P \Big/ \left(\frac{\partial \ln V}{\partial T}\right)_P = \left(\frac{\partial \ln\epsilon}{\partial p}\right)_T \Big/ \left(\frac{\partial \ln V}{\partial p}\right)_T.$$

In Table III this relation is tested for LiF, NaCl, and KCl. The agreement is poor, indicating that even for these simple materials the dielectric constant cannot be considered to be a function of the volume alone.

TABLE II.* Values of $-(\partial \ln\epsilon/\partial p)_T$ at room temperature and atmospheric pressure.

Substance		Room temp. (°C)	$-(\partial \ln\epsilon/\partial p)_T \times 10^5$ bars	Average $-(\partial \ln\epsilon/\partial p)_T \times 10^5$ bars
MgO		30	0.320	0.320±0.019
LiF	*a*	28	0.440	0.448±0.028
	b	29	0.456	
NaCl	*a*	25	0.994	0.98±0.06
	b	30	0.975	
KCl	*I*	29	1.00	1.05±0.08
	II	28	1.10	
KBr		26	1.17	1.17±0.09

* The alkali halides and the magnesium oxide used in these measurements were obtained from the Harshaw Chemical Company and the Norton Company, respectively.

TABLE III.* The dependence of ϵ on the volume.

	$(\partial \ln\epsilon/\partial T)_P\alpha^{-1}$	$-(\partial \ln\epsilon/\partial p)_T a^{-1}$
LiF	3.57	2.95
NaCl	2.84	2.30
KCl	3.15	1.86

* Values of $(\partial \ln\epsilon/\partial T)_P$, the thermal expansion coefficient α, and the compressibility, a, are given in Table I.

IV. COMPARISON WITH THEORY

Many writers have considered the dielectric properties of ionic crystals.[10] In particular, Mott and Littleton[11] present a point of view which is useful in discussing the measurements reported here. This theory is an extension of the ideas of Heckmann,[12] and is in many ways similar to the discussion of Hojendahl.[13]

Mott and Littleton derive the equation

$$\frac{\epsilon-1}{4\pi}=\frac{8\pi\beta\beta_0(\gamma-1)/3+(\beta+\beta_0)}{1-4\pi(\beta+\beta_0)/3+16\pi^2\beta\beta_0(1-\gamma^2)/9}, \tag{1}$$

where ϵ is the dielectric constant, β_0 is the polarizability of the electrons of the ions per unit volume, β is the polarizability of the lattice per unit volume and γ is called here the constant of the inner field. The quantity γ has the value unity when the inner field can be described by the Lorentz field, which is the case in the NaCl type structure if there is no overlap between adjacent ions; it is defined by an equation of the type

$$F=E+4\pi\gamma P/3, \tag{2}$$

where F is the effective polarizing field, E is the electric field in the medium and P is the total polarization per unit volume. The paper of Mott and Littleton should be consulted to see the particular manner in which they introduce γ.

At optical frequencies when the lattice polarizability vanishes, Eq. (1) can be written in the familiar Lorentz-Lorenz form

$$(\epsilon_0-1)/(\epsilon_0+2)=4\pi\beta_0/3, \tag{3}$$

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[10] For general discussions see N. Born and M. Goeppert-Mayer, Handb. d. Phys. **24/2**, 759 (1933) and N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chapter 1. For discussions concerning the optical dielectric constant see: K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924). K. F. Herzfeld and K. L. Wolf, Ann. d. Physik (4) **78**, 35 and 195 (1925). H. Mueller, Phys. Rev. **47**, 947 (1935). W. Shockley, Phys. Rev. **70**, 105 (1946). For discussions concerning the low frequency dielectric constant see: G. Heckmann, Zeits. f. Krist. **61**, 250 (1925). A. Eucken and A. Buchner, Zeits. f. physik. Chemie (13) **27**, 321 (1934). N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938). K. Hojendahl, K. Danske Vidensk Selskab. 16, No. 2 (1938). S. Roberts, Phys. Rev. **76**, 1215 (1949). For discussions of the infra-red eigenfrequency see: M. Born and E. Brody, Zeits. f. Physik **11**, 327 (1922). R. B. Barnes, Zeits. f. Physik **75**, 732 (1932). J. A. Wasastjerna, Soc. Sc. Fennica. Com. Phys. Mat. **8**, No. 20 (1935). R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938).

[11] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[12] G. Heckmann, Zeits. f. Krist. **61**, 250 (1925).

[13] K. Hojendahl, K. Danske Vidensk. Selskab **16**, No. 2 (1938).

TABLE IV.* Calculated data on γ and $(\partial\gamma/\ln\rho)_T$.

	γ	$(\partial\gamma/\partial\ln\rho)_T$	$\frac{\Delta\epsilon\gamma}{\Delta\epsilon}$	γ_H	$(\partial\gamma_H/\partial\ln\rho)_T$	$\frac{\Delta\epsilon\gamma_H}{\Delta\epsilon}$
LiF	0.25	-0.5 ± 1.0	0.1	0.73	-0.5 ± 0.3	0.4
NaCl	-0.08	-0.4 ± 1.3	0.1	0.47	-1.0 ± 0.5	0.5
KCl	-0.05	-3.0 ± 1.0	0.6	0.46	-1.8 ± 0.4	0.8
KBr	-0.04	-2.2 ± 0.7	0.5	0.42	-1.7 ± 0.5	0.8

* γ and $(\partial\gamma/\partial\ln\rho)_T$ are calculated from the theory of Mott and Littleton; γ_H and $(\partial\gamma_H/\partial\ln\rho)_T$ from the theory of Hojendahl. Data for the calculation are given in Tables I and II. The part of the total change of ϵ which is attributed to the change of the inner field is listed in the third and sixth columns.

TABLE V.* The relative discrepancy between ν calculated by means of Eqs. (10) and (12) and the measured eigenfrequency ν_M.

	$(\nu_M-\nu)/\nu_M$
LiF	0.05
NaCl	0.09
NaBr	0.07
NaI	0.07
KCl	0.09
KBr	0.07
KI	0.11

* Data for the calculation are taken from summaries of experimental data by Hojendahl (reference 12) except for the compressibilities which are taken from F. Birch, Geological Society of America, Special Papers No. 86, 52, (1942).

where ϵ_0 is the square of the optical refractive index. Equation (3) is used to determine values of β_0. At frequencies below the characteristic frequency of the lattice the lattice polarizability per unit volume exists and is defined as

$$\beta=N(Ze)^2/R, \tag{4}$$

where Ze is the ionic charge, N is the number of ion pairs per unit volume, and R times the relative displacement of the positive ions with respect to the negative ions is the repulsive overlap force resisting this displacement. If the values of β_0 and β, as given by Eqs. (3) and (4), are substituted into Eq. (1), one finds the relation

$$\frac{\epsilon-1}{\epsilon+2}=\frac{(\epsilon_0+2)/(\epsilon_0-1)+3R/4\pi N(Ze)^2-2(1-\gamma)}{(\epsilon_0+2)/(\epsilon_0-1)[3R/4\pi N(Ze)^2]-(1-\gamma)^2}. \tag{5}$$

For many ionic crystals, Mott and Littleton have calculated R for the cases $\gamma=0$ and $\gamma=1$. They compare these values of R with R as calculated from the Born-Mayer potential between nearest neighbors, and find that the agreement is far better for the case $\gamma=0$ than it is for $\gamma=1$.

Mott and Littleton also re-derive a relation given by Heckmann[12] connecting the infra-red eigenfrequency, ν, with the dielectric constants and γ. This equation is

$$\epsilon-\epsilon_0=(Ne^2/\pi M\nu^2)[1+\tfrac{1}{3}\gamma(\epsilon_0-1)]^2, \tag{6}$$

where M is the reduced mass of a positive and a negative ion. If in Eq. (6) $\gamma=0$, the familiar equation of Born[14] is obtained.[15] From Eq. (6) Mott and Littleton compute γ for several ionic crystals from the measured dielectric constants and eigenfrequencies. These values of γ are also much closer to zero than to unity. Mott and Littleton attribute this decrease of γ from the Lorentz value of one to the interpenetration of nearest neighbor ions.[16]

The pressure dependence of all quantities entering Eq. (5) except γ has been measured, or can be estimated independently of the dielectric constant. By using Eq. (5) to calculate the change in γ with pressure from the change in the dielectric constant with pressure, the theory can be checked in a qualitative way as follows. According to the picture of Mott and Littleton, γ is less than unity because of the overlap of neighboring ions; the effect of high pressures is to reduce the inter-ionic distance and increase the overlap; therefore, γ should decrease with increasing pressure.

(A) The Repulsive Force Constant at High Pressure

Before the change of γ with pressure can be calculated from Eq. (5), it is necessary to know the change in the repulsive force constant R with pressure in addition to the pressure dependence of ϵ, ϵ_0, and N. Since R cannot be measured directly, it must be related to the elastic constants or to the compressibilities because the pressure dependence of these quantities have been measured.

Equation (6), which relates γ to the dielectric constants and to the eigenfrequency ν is not used to calculate the change in γ with pressure because the pressure variation of ν has not been measured. Furthermore, there seems to be no precise way by which ν can be related to the elastic properties independently of γ and of the dielectric constant.

For a lattice under zero external pressure, the repulsive force constant R has been related to the compressibility x and the interionic distance, L, by Hojendahl.[17] An obvious extension of Hojendahl's calculation for the case of a lattice under external pressure p, yields the relation

$$R=6L/x-8pL \tag{7}$$

for the NaCl type lattice. This result was obtained with the assumption that the overlap interaction energy acts only between nearest neighbors and is a function only of the distance between the ions. Furthermore, it is assumed that the lattice is at the absolute zero of tem-

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[14] M. Born and M. Goeppert-Mayer, Handb. d. Phys. **24**/2, 646 (1933).

[15] In Eq. (10), ν corresponds to the characteristic transverse frequency of long wave-length. Since the low frequency dielectric constant ϵ is usually measured in a parallel plate condenser, one might wonder if the dielectric constant should be related to the characteristic frequency of longitudinal polarization waves. This point is discussed by R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 861 (1938), and they show that ν is properly the transverse frequency.

[16] Mott and Littleton, reference 11, or Mott and Gurney, reference 10, p. 16.

[17] K. Hojendahl, K. Danske Vidensk. Selskab, **16** (No. 2), 110 (1938).

perature. If values of the lattice constant and compressibility at high pressures are substituted in Eq. (7), it is found that R increases with pressure. Hence by Eq. (4) the lattice polarizability decreases with increasing pressure.

(B) The Calculation of γ and $(\partial\gamma/\partial \ln\rho)_T$

When the values of $N=L^{-3}/2$ and R for the NaCl type structure are substituted into Eq. (5), we have

$$(1-\gamma)=\frac{\epsilon+2}{\epsilon-1}\left\{1\pm\left[\left(\frac{\epsilon-1}{\epsilon+2}\right)\left(\frac{\epsilon_0+2}{\epsilon_0-1}\right)-1\right]^{\frac{1}{2}}\times\left[\left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{9L^4(1-4px/3)}{\pi(Ze)^2x}-1\right]^{\frac{1}{2}}\right\}. \quad (8)$$

Table IV gives the values of γ at zero pressure calculated from Eq. (8) by using the negative root. The positive root is rejected because when the eigenfrequency ν is calculated by elimination of γ from Eqs. (6) and (8) the negative root alone yields values of ν which are physically plausible. In Table V are listed the percentage discrepancies between valances of ν calculated in this way and the eigenfrequency ν_M measured by Barnes and Czerny.[18] This comparison, in addition to indicating the proper sign in Eq. (12), may serve to give some additional justification to the use of γ, a quantity whose physical meaning is somewhat ambiguous.

From Table IV it is seen that γ is nearer to zero than to the Lorentz value of unity, which Mott and Littleton concluded using the Born-Mayer repulsion to calculate the repulsive force. In the case of MgO, an imaginary value of γ is obtained from Eq. (8). This result may arise from the assumption of central forces in the calculation of the repulsive force constant for MgO or the neglect of next nearest neighbor interactions.

For comparison with the values of γ calculated from the theory of Mott and Littleton, the values of γ calculated by the theory of Hojendahl[19] are listed in Table IV where they are denoted by γ_H. The values of γ_H, as well as the values of γ, are less than unity at zero pressure. There is very poor correlation between the degree of ionicity in the crystals and the values of the γ's as calculated from the theories. For example, since the value of γ is nearer to unity in LiF than in NaCl, there should be less overlap in LiF than in NaCl, and hence LiF should be more ionic than NaCl. However, NaCl is known to be more ionic than LiF. As Hojendahl has remarked, part of the cause of the anomalously large value of the constant of the inner field calculated for lithium salts is that the theory has neglected the overlap between negative ions, and in lithium salts this effect is important.

The constant of the inner field, as used by Hojendahl, is really only an adjustable parameter, while Mott and Littleton try to give it some physical significance in their theory. For this reason, and because the theory of Mott and Littleton reduces to the accepted Lorentz-Lorenz relation, Eq. (3), for the optical dielectric constant while the theory of Hojendahl does not, we have given the preference in this paper to the theory of Mott and Littleton.

Since in both theories the inner field is less than the Lorentz value at zero pressure, one might expect the inner field to decrease further from the Lorentz value of one at high pressure. In Table IV are listed values of the change of γ with density, which are obtained by differentiation of Eq. (8), and also values which are obtained by differentiation of Hojendahl's Eq. (75),[20] in which x is replaced by $x(1-(4/3)px)^{-1}$. The calculated change of γ with respect to the density is negative in all cases.

(C) Discussion

The values of $(\partial\gamma/\partial \ln\rho)_T$ indicate that γ decreases more rapidly in materials of high compressibility than in those of low compressibility. However, it is dangerous to attach too much significance to the numerical values of this coefficient since these values are very sensitive to the quantity b which is determined from volume measurements at high pressures through the equation

$$-\Delta V/V_i=ap-bp^2, \quad (9)$$

where ΔV is the change in volume, V_i is the initial volume, and a and b are constants to fit the data. Of course, b can also be related to data on the pressure dependence of the elastic constants. We believe that the values of b which are obtained from the elastic constant measurements of Lazarus[8] by a single differentiation of the data, are more reliable than those obtained from volume measurements by two differentiations of the data. Unfortunately, elastic constant measurements have been made only on NaCl and KCl. For other salts the only values of b available are from volume measurements (see Table I).

Since $(\partial\gamma/\partial \ln\rho)_T$ is very sensitive to the value of b used in the calculation, one should inquire whether the errors in b are sufficiently large to cause uncertainty in the sign of $(\partial\gamma/\partial \ln\rho)_T$. The errors in the values of $(\partial\gamma/\partial \ln\rho)_T$ are calculated from an assumed error in b of 5 percent and from the error in $(\partial \ln\epsilon/\partial p)_T$ listed in Table II. The precision of b appears better than 5 percent. However, the main uncertainty comes rather from the assumption that the volume at the high pressures can be represented by the two parameter equation, Eq. (9). In fact, Bridgman's recent measurements[21] at very high pressures indicate that b itself is a function of pressure.

The errors in $(\partial\gamma/\partial \ln\rho)_T$ listed in Table IV indicate that no definite conclusion can be made concerning the

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[18] R. B. Barnes, Zeits. f. Physik **75**, 732 (1932).

[19] Reference 17, p. 116. Hojendahl uses the symbol β_K instead of γ_H used here.

[20] Reference 17, p. 112.

[21] F. Birch, Geological Society of America, Special Papers, No. 86, 52 (1942).

sign of this coefficient for LiF and NaCl, as calculated from the theory of Mott and Littleton. In all the other cases its sign is well established as negative, and the calculations indicate that the contribution to the decrease of the low frequency dielectric constant from the decrease of the inner field is large. This is shown by the values of $\Delta\epsilon_\gamma/\Delta\epsilon$ listed in the third and sixth columns of Table IV.

V. CONCLUSION

The low frequency dielectric constant of ionic crystals was measured at high pressures and found to decrease with increasing pressure. The existing lattice theories explain this decrease as arising not only from the decrease in the lattice polarizability produced by the increase of the repulsive forces but also because the increasing overlap of adjacent ions at high pressures reduces the internal field.

In contradistinction to liquids and gases, the change in density of ionic crystals plays a minor role compared to the change in overlap in affecting the low frequency dielectric constant.

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A Simplified Method of Computing the Cohesive Energies of Monovalent Metals

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A method is developed which, within the limits of the spherical cell approximation first presented by Wigner and Seitz, permits the evaluation of the cohesive energy, lattice constant, and compressibility of a monovalent metallic solid without the explicit computation of a central field for the atom. It is shown that empirical values of the first few s and p levels of the free atom can supply the relevant information usually obtained through the computation of a central field, so that a considerable simplification is possible. The method is applied to the calculation of the usual solid state parameters for the alkali metals, Na, K, and Rb. The results for Na compare very favorably with experiment as well as with those gained by previous workers. The K and Rb computations agree decidedly less well with experiment, but the values for K are appreciably better than those previously computed utilizing an explicit central field. The errors shown by the K and Rb computations are believed to be the inevitable consequence of any theory derived by replacing the effect of the core electrons by an equivalent central field rather than a result of any peculiarities inherent in the present approach.

I. Introduction: In the well-known s-sphere approximation developed by Wigner and Seitz[1] for the computation of the physical parameters of metallic lattices the ground-state energy of the solid is the lowest eigen-energy, ϵ_0, of the equation

$$\frac{d^2U^{(l)}}{dr^2}+\left[\epsilon-V(r)-\frac{l(l+1)}{r^2}\right]U^{(l)}=0, \tag{1}$$

solved with $l=0$ subject to the boundary conditions that $U^{(0)}$ be zero at the origin and that

$$\left[r\frac{dU^{(0)}}{dr}\right]_{r=r_s}=U^{(0)}(r_s). \tag{2}$$

In these equations the radius, r, is measured in Bohr units and the energy, ϵ_0, in Rydberg units. The quantity r_s is the radius of the s-sphere and is related to the lattice parameter, d, of a body-centered cubic lattice like that of the alkali metals by the equation

$$d=(8\pi/3)^{\frac{1}{3}}r_s. \tag{3}$$

The potential $V(r)$ is taken to be identical with that of the free atom, so that (1) is just the radial wave equation of the free atom.

In addition to its ground-state energy the solid possesses a mean Fermi energy which, at absolute zero, is given by

$$\epsilon_F=\frac{9\pi}{10}\left(\frac{3}{2\pi}\right)^{\frac{1}{3}}\frac{\alpha}{r_s^2}=\frac{2.21\alpha}{r_s^2}, \tag{4}$$

where α is a constant which Bardeen[1] has shown is

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[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935). This outline of the method follows the development presented by J. Bardeen, J. Chem. Phys. **6**, 367 (1938).