

Pressure and Temperature Dependence of the Static Dielectric Constants of KCl, NaCl, LiF, and MgO

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The static dielectric constants and their pressure derivatives of KCl, NaCl, LiF, and MgO have been measured at several temperatures ranging from 15 to 295 °K. The samples were prepared in the form of three-terminal parallel-plate capacitors and the dielectric constants were determined from measurements of the capacitance with a high-precision bridge. In all cases the dielectric constants decrease with temperature as does the magnitude of the pressure dependence. Effects of permanent-dipole impurities in NaCl were seen at temperatures around 20 °K. The data were used to calculate the fixed-volume temperature derivative of the dielectric constants. This quantity $(\partial\epsilon/\partial T)_V$, apparently exhibiting the effects of lattice anharmonicity, has a similar temperature dependence for all four compounds: It increases from its room-temperature value as the temperature is lowered, reaches a maximum value at $T/\Theta_D \approx 0.15$ (Θ_D = Debye temperature), and then decreases rapidly toward zero at lower temperatures.

I. INTRODUCTION

The origin of the static dielectric constant of an ionic crystal is due to two contributions of similar magnitude: an "electronic" or "optical" part due to the polarization of the ionic charge clouds and a "lattice" part due to the relative shift of the oppositely charged ionic sublattices. The two effects can be separated since at optical frequencies only the electronic mechanism is active and index of refraction measurements determine its magnitude. The lattice contribution can be related to other lattice properties and Szigeti¹ has developed such a relationship with the bulk modulus. Deviations between this relation and experimental results are accounted for by assigning an effective charge e^* to the ions. There have recently appeared many extensions of this work, some inspired by Phillips's² results in crystal ionicity. Some authors^{3,4} have extended these studies to the pressure dependence of the effective ionic charge and for such studies it is important to have experimental data on the temperature and pressure derivatives of both the optical and static dielectric constants.

The temperature dependence of the dielectric constant at fixed volume is a direct anharmonic effect and is thus useful in studies of lattice anharmonicity. This quantity, though not directly measurable, can be obtained from the measured temperature and pressure dependence of the dielectric constant. The nature of the various theoretical models makes the dielectric data particularly useful if it is applicable to a wide temperature range including the vicinity of absolute zero. For the above reasons it appears that experimental data like that pre-

sented in this work should be useful in extending the understanding of ionic compounds.

There have recently appeared several papers reporting measurements on the temperature dependence of the dielectric constants of alkali halides and some reporting measurements on their pressure dependence. However, the pressure data have been limited to room-temperature results. In this work the pressure-dependence measurements were made from room temperature down to as low as 15 °K.

The materials chosen for this study were NaCl, KCl, LiF, and MgO. The first two were selected since they are usually considered "typical" alkali halides. LiF was selected since it often exhibits atypical alkali-halide behavior and also since it has a high Debye temperature. A wide range of Debye temperatures was considered with the hope that the data would then be more useful in studies of lattice effects. MgO also has a high Debye temperature and it was thought that the experimental results might be useful for a comparative study between this alkaline earth oxide and the closely related alkali halides.

II. EXPERIMENT

The materials investigated were single crystals of NaCl, KCl, and LiF from Harshaw Chemical Co. and MgO from Semi-Elements, Inc. The samples were in the form of circular disks of nominal size 30 mm in diameter and 1 mm in thickness. The surfaces were polished flat and parallel to within 0.005 mm. Aluminum electrodes were deposited directly on the crystal surfaces by evaporation in vacuum. A thin shadow ring was placed on one

side of the sample during this process to achieve the narrow gap between the active center electrode and the guard ring necessary for three-terminal capacitance measurements. The diameter of the center electrode and the width of the gap were measured with a traveling microscope. The width of the gap was just under 0.17 mm.

The sample was placed in a sample holder which maintained the shielding of the active leads and then placed directly in the pressure vessel. Two electrical leads were run from the pressure vessel through 1.6-mm-o.d. pressure tubing to a room-temperature location where they were brought out of the pressure system using standard conical lead-outs with plastic insulating cones. The pressure vessel itself was used for electrical contact to the guard electrode. Helium gas was used as the pressure fluid with the pressure generated by an air-operated gas compressor and measured by means of one or more Bourdon-tube pressure gauges.

The pressure vessel was installed in a controlled-temperature Dewar which for this system allowed measurements over a continuous temperature range from about 10 °K to room temperature. Once the system reached thermal equilibrium no measurable temperature variation at the sample was noted. Temperature measurements were made with platinum and germanium resistance elements and are accurate to 0.1 °K. The procedure was to pressurize the system to about 2 kbar and then allow several hours to achieve thermal equilibrium at the desired temperature. Capacitance measurements were then made at various points of decreasing pressure while the system was maintained at constant temperature. On several occasions measurements were made for increasing as well as decreasing pressures and no hysteresis was observed.

The dielectric constant and its change with pressure and temperature were determined from mea-

surements of the capacitance of the parallel-plate capacitor as a function of pressure and temperature. Since the dielectric constant of an ionic crystal is relatively insensitive to frequency in the low-frequency range the measurements were carried out primarily at the single frequency of 1 kHz with some measurements being made at 10 kHz. No significant change in the reported values of the dielectric constant resulted from this frequency variation. Capacitance measurements were made with a General Radio model 1620A capacitance measuring assembly which yields capacitance measurements to six figures. The three-terminal measurement method allows capacitance determinations which are independent of lead capacitance and hence reflect only the variation of the sample capacitance with pressure and temperature.

III. RESULTS

Thermal expansion and elastic data are needed over the entire temperature range of the measurements in order to reduce the measured quantities to values of the dielectric constants and their pressure derivatives. The literature sources of this auxiliary data are as follows: thermal expansion coefficient, NaCl,⁵ KCl,⁶ LiF,⁶ MgO⁷; isothermal bulk modulus, NaCl,^{8,9} KCl,^{8,10} LiF,^{11,12} MgO.⁷

The results of the present experiments for NaCl, KCl, LiF, and MgO are shown in Tables I, II, III, and IV, respectively. The first column of these tables represents the temperatures at which the measurements were made and the second column represents values of the dielectric constant which were obtained from capacitance values and the dimensions of the capacitor. Corrections for the gap between the center electrode and the guard ring were taken into account by adding one half the area of this gap to the area of the capacitor.^{13,14}

The dielectric constants of these four materials have been measured at room temperature by numerous investigators and we find no serious discrepancies with our values. For two of the compounds data exists for comparison over the entire temperature range of our measurements. Robinson and Hallett¹⁵ have measured the dielectric constants of NaCl and KCl from 4.2 to 300 °K. Our values of ϵ for NaCl are essentially identical to theirs at all temperatures. For KCl, our values follow theirs with temperature change, except for a systematic difference of about $\frac{1}{2}\%$. This difference is most likely due to errors in measurements of capacitor dimensions. There is some discrepancy at the very lowest temperatures and this will be discussed below.

Experimental values of the constant-pressure temperature derivatives of the static dielectric constants are listed in the third columns of Tables I-IV. Throughout most of the temperature range

TABLE I. Results of the dielectric constant temperature-pressure measurements expressed in several forms for NaCl. All quantities shown are evaluated at zero pressure.

T (°K)	ϵ	$(\partial\epsilon/\partial T)_P$ ($10^{-4}/^\circ\text{K}$)	$(\partial \ln\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial \ln\epsilon/\partial \ln\gamma)_T$ γ = lattice const.
295	5.893	19.1	-1.03	-6.09	7.25
210	5.740	17.8	-0.95	-5.48	7.08
190	5.704	17.6	-0.94	-5.34	7.07
170	5.670	17.2	-0.92	-5.22	7.01
150	5.636	16.8	-0.91	-5.12	7.01
130	5.603	16.5	-0.89	-5.01	7.00
110	5.571	15.9	-0.88	-4.91	7.00
90	5.539	15.1	-0.87	-4.82	7.00
70	5.510	13.6	-0.85	-4.71	6.94
50	5.484	10.3	-0.84	-4.62	6.88
30	5.468	3.3	-0.83	-4.54	6.80
16	5.471	-4.4	-0.88	-4.79	7.18

TABLE II. Results of the dielectric constant temperature-pressure measurements expressed in several forms for KCl. Except for the 15 °K data, all quantities shown are evaluated at zero pressure.

T (°K)	ϵ	$(\partial\epsilon/\partial T)_P$ ($10^{-4}/^\circ\text{K}$)	$(\partial \ln\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial \ln\epsilon/\partial \ln r)_T$ $r = \text{lattice const.}$
295	4.860	14.0	-1.26	-6.13	6.55
210	4.736	13.1	-1.15	-5.44	6.30
190	4.709	12.9	-1.11	-5.23	6.16
170	4.682	12.6	-1.08	-5.04	6.05
150	4.656	12.4	-1.07	-4.98	6.07
130	4.630	12.1	-1.04	-4.82	5.98
110	4.607	11.8	-1.02	-4.71	5.94
90	4.583	11.3	-1.00	-4.60	5.90
70	4.560	10.5	-1.00	-4.55	5.93
50	4.537	9.0	-0.99	-4.47	5.89
30	4.517	7.4	-0.96	-4.31	5.73
15	4.509	4.3	-0.94	-4.24	5.66

investigated our NaCl and KCl data agree very well with those of Robinson and Hallett¹⁵ and the temperature derivatives are taken from their work. The $(\partial\epsilon/\partial T)_P$ values for LiF and MgO were obtained from our own ϵ - T data either graphically or, where smoothness of the data permitted, by fitting a second degree curve to ϵ vs T . Our room-temperature value of $(\partial\epsilon/\partial T)_P$ for LiF agrees to about 2% with the recent results of Fontanella, Andeen, and Schuele.¹⁶ The MgO $(\partial\epsilon/\partial T)_P$ value at 295 °K in Table IV is only about one half that reported by Krishnan,¹⁷ however, our result does agree to about 10% with that of Bosman and Havinga.¹⁸

The fourth, fifth, and sixth columns of Tables I-IV express the results of the pressure measurements on the four compounds. Remarks on the reduction of the data to these numbers follows.

A raw-data plot of capacitance versus pressure is shown in Fig. 1. This particular graph for NaCl at 180 °K is typical and shows the nearly linear decrease of capacitance with pressure that was

TABLE III. Results of the dielectric constant temperature-pressure measurements expressed in several forms for LiF. Except for the 30 and 15 °K data, all quantities shown are evaluated at zero pressure.

T (°K)	ϵ	$(\partial\epsilon/\partial T)_P$ ($10^{-4}/^\circ\text{K}$)	$(\partial \ln\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial \ln\epsilon/\partial \ln r)_T$ $r = \text{lattice const.}$
295	9.073	25.0	-0.51	-4.6	10.2
210	8.858	24.6	-0.45	-4.0	9.3
190	8.809	24.3	-0.45	-4.0	9.4
170	8.764	23.6	-0.45	-3.9	9.5
150	8.716	22.5	-0.44	-3.9	9.5
130	8.675	20.8	-0.45	-4.0	9.8
110	8.634	18.5	-0.42	-3.6	9.1
90	8.601	15.5	-0.45	-3.9	9.8
70	8.571	11.6	-0.43	-3.7	9.4
50	8.555	6.8	-0.43	-3.7	9.5
30	8.550	0.9	-0.47	-4.1	10.4
15	8.547	0	-0.43	-3.7	9.6

TABLE IV. Results of the dielectric constant temperature-pressure measurements expressed in several forms for MgO. All quantities shown are evaluated at zero pressure.

T (°K)	ϵ	$(\partial\epsilon/\partial T)_P$ ($10^{-4}/^\circ\text{K}$)	$(\partial \ln\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial\epsilon/\partial P)_T$ ($10^{-2}/\text{kbar}$)	$(\partial \ln\epsilon/\partial \ln r)_T$ $r = \text{lattice const.}$
295	9.958	9.8	-0.18	-1.79	8.92
210	9.876	9.5	-0.18	-1.82	9.30
190	9.857	9.1	-0.18	-1.75	9.00
170	9.839	8.5	-0.17	-1.68	8.68
150	9.823	7.7	-0.17	-1.70	8.85
130	9.808	6.7	-0.16	-1.60	8.36
110	9.797	5.3	-0.17	-1.66	8.67
90	9.788	3.5	-0.17	-1.69	8.89
70	9.783	1.4	-0.17	-1.71	8.99
50	9.782	0	-0.18	-1.72	9.03

observed in practically all cases. The line shown on the graph is the tangent to the curve at zero pressure; and, since the derivatives desired are those evaluated at zero pressure, it is the slope of this line that is used in the calculations. The numerical values of these slopes were found from least-squares parabolic fits to the data.

An exception to the above method was made in the cases of the pressure runs for KCl at 15 °K and for LiF at 15 °K and at 30 °K. In these cases the capacitance changed slowly and nonlinearly with pressure at low pressures but then assumed linear behavior at higher pressures. These slopes were found by fitting a straight line to the higher-pressure linear data points.

The capacitance change occurring upon the application of pressure is due not only to the change

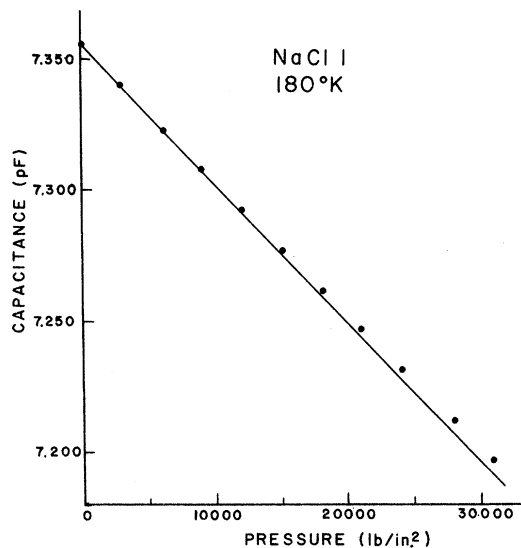


FIG. 1. Raw-data plot of sample capacitance vs pressure. Data shown are for NaCl at 180 °K. The line shown is the tangent to the curve at zero pressure as determined by a parabolic least-squares fit.

in dielectric constant, but also is due partly to changes in capacitor dimensions. The two effects can be separated by using the following expression:

$$\left(\frac{\partial \ln C}{\partial P}\right)_T = \left(\frac{\partial \ln \epsilon}{\partial P}\right)_T - \frac{1}{3B_T}, \quad (1)$$

where C is capacitance, ϵ is the dielectric constant, P is pressure, T is temperature, and B_T is the isothermal bulk modulus.

The fourth column in Tables I–IV represents the fractional change in dielectric constant per unit change in pressure and these values result from Eq. (1). The fifth column results simply from $(\partial \epsilon / \partial P)_T = \epsilon (\partial \ln \epsilon / \partial P)_T$. The last column in the tables represents the ratio of a fractional change in dielectric constants to a fractional (isothermal) change in crystal dimensions. These numbers result from the relationship $(\partial \ln \epsilon / \partial \ln r)_T = -3B_T \times (\partial \ln \epsilon / \partial P)_T$.

The primary source of error in the ϵ values is the measurement of the capacitor dimensions. Considering the measurements involved, we believe the error in the ϵ values to be of the order of $\frac{1}{2}\%$. From data repeatability and from consideration of the instrumentation we set an error of 2% on the pressure measurements. For some unknown reason there was considerably greater scatter in the LiF data than in that for the other three materials and consequently the above errors are probably too optimistic for that compound. More reasonable errors for LiF would be 2% in the case of ϵ and 10% in the case of $(\partial \epsilon / \partial P)_T$.

The pressure derivatives of ϵ have been measured at room temperature by several investigators and our values are compared with the others in Table V. The only striking disagreement occurs in the case of KCl. Our value is considerably greater in magnitude than the others. For this

TABLE V. Comparison with other pressure work. Shown are room temperature results for $(\partial \ln \epsilon / \partial P)_T$ in units of 10^{-2} kbar $^{-1}$.

Work	NaCl	KCl	LiF	MgO
Present	-1.03	-1.26	-0.51	-0.18
Mayburg ^a	-0.98	-1.05	-0.45	-0.32
Jones ^b	-1.01	-1.09	-0.50	...
Bosman and Havinga ^c	-0.91	-0.97	...	-0.19
Gibbs and Jarman ^d	-0.98	-1.01	-0.34	...
Hill ^e	-0.49	-0.16
Fontanella, Andeen, and Schuele ^f	-1.04	-1.10	-0.51	...

^aS. Mayburg, Phys. Rev. **79**, 375 (1950).

^bB. W. Jones, Phil. Mag. **16**, 1085 (1967).

^cReference 18.

^dD. F. Gibbs and M. Jarman, Phil. Mag. **7**, 663 (1962).

^eG. J. Hill, Nature **193**, 1275 (1962).

^fReference 16.

reason the experiment was repeated, but the same results were obtained.

Figure 2 displays, as a function of temperature, the magnitude of the fractional change in ϵ per unit change in pressure. If the four compounds under consideration are placed in the order of increasing compressibility, the resulting sequence is MgO-LiF-NaCl-KCl. As might be expected this is also (at any given temperature) the ordering of the magnitude of $(\partial \ln \epsilon / \partial P)_T$. For example, at 300° K, the dielectric constant of MgO decreases at a rate of 0.2% per kbar, while for the more compressible KCl the corresponding rate is 1.2% per kbar. Likewise, Fig. 2 shows that the size of the effect of temperature on $(\partial \ln \epsilon / \partial P)_T$ is in the same order; for example, over the temperature range studied, the magnitude of $(\partial \ln \epsilon / \partial P)_T$ remains essentially constant for MgO while for the more compressible KCl it decreases by about 25%. The rise in the curve for NaCl at very low temperatures will be discussed later.

IV. DISCUSSION

A. Low-Temperature Minimum in NaCl

The dielectric constant of NaCl was found to have a minimum at about 25° K; and, as Fig. 2 shows, an extremum in the pressure derivative of the dielectric constant was also found at about that same temperature. This effect is undoubtedly due to impurity ions having permanent electric dipole moments (such as OH⁻). Robinson and Hallett¹⁵ and Rejler, Wernberg, and Beckman¹⁹ also found low-temperature minima while studying the temperature dependence of the dielectric constant of alkali halides. Kanzig, Härt, and Roberts²⁰ have extensively studied the low-temperature dielectric behavior of alkali halides which were deliberately doped with hydroxyl ions. They find that, as temperature is decreased, the dielectric constant decreases to a minimum, increases to a maximum, and then decreases again. However, they do not find such behavior in very pure zone-refined specimens.

Though we cannot be certain, we suspect that we were just beginning to measure impurity effects in KCl at our lowest available temperatures. No such effects were evident in the LiF and MgO samples.

The physical process occurring, of course, is that as the lattice thermally quiets down the permanent dipoles can more readily align with the electric field and thus contribute appreciably to the total dielectric constant of the crystal. With this picture in mind, it is reasonable to expect the pressure dependence of the dielectric constant to behave qualitatively as shown for NaCl in Fig. 2. Compressing the lattice will hinder the rotation of these dipoles and render them less effective in

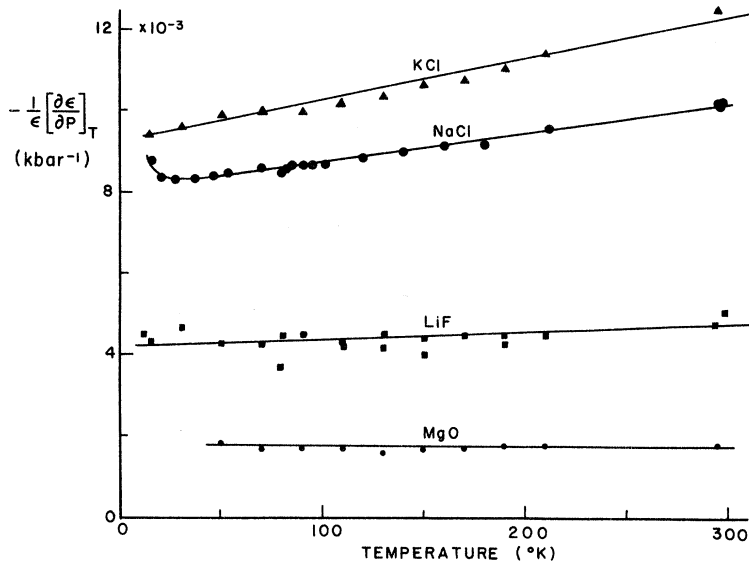


FIG. 2. Logarithmic pressure derivative of the dielectric constant as a function of temperature for KCl, NaCl, LiF, and MgO. The points indicate the temperatures at which the pressure data were taken and the values of $(\partial \ln \epsilon / \partial P)_T$ derived from that data.

contributing to the electric polarizability. Therefore as these dipoles account for a relatively greater share of ϵ , $\partial \epsilon / \partial P$ should become more negative.

B. Constant-Volume Temperature Dependence

The constant-volume temperature dependence of an ionic crystal's dielectric constant is an interesting quantity since it is directly related to lattice anharmonicity. At constant volume the electronic polarizability should not depend on temperature and, if the interionic forces are harmonic, neither should the lattice polarizability. Direct measurement of $(\partial \epsilon / \partial T)_V$ is not possible but its value may be determined if $(\partial \epsilon / \partial T)_P$ and $(\partial \epsilon / \partial P)_T$ are known. The appropriate relationship is

$$(\partial \ln \epsilon / \partial T)_P = (\partial \ln \epsilon / \partial T)_V - \beta B_T (\partial \ln \epsilon / \partial P)_T, \quad (2)$$

where β is the volume coefficient of thermal expansion and B_T is the isothermal bulk modulus. Table VI gives the relative size of the three terms in this relation. The first and third columns are derived from measured quantities and the middle column is determined using Eq. (2).

Figure 3 shows $(\partial \ln \epsilon / \partial T)_V$ as a function of temperature for the four materials under consideration. At room temperature, except for LiF, this quantity is positive; it then in all cases increases toward a maximum positive value at lower temperatures, and finally, except for NaCl, approaches zero near absolute zero. The negative $(\partial \ln \epsilon / \partial T)_V$ for NaCl at very low temperatures is an impurity effect which will be discussed below.

Positive values of $(\partial \ln \epsilon / \partial T)_V$ would not be expected from a simple anharmonic model with no ion overlap. If the "force constants" increased with increasing ionic separation, raising the tempera-

ture would then lead to an effective increase in these force constants which in turn would make the ionic lattice less polarizable, or in other words, would lead to negative values of $(\partial \ln \epsilon / \partial T)_V$. However, Fuchs,²¹ following the work of Szigeti,²² was able to account for a positive $(\partial \ln \epsilon / \partial T)_V$. He used a lattice dynamics approach considering both anharmonic terms in the lattice potential and higher-order electric dipole effects due to ionic overlap. The result is two competing anharmonic terms one of which gives a positive contribution and the other a negative contribution to $(\partial \ln \epsilon / \partial T)_V$. In this theory then the sign of $(\partial \ln \epsilon / \partial T)_V$ is determined by which of the two terms dominate. Though explicit numerical calculations were not possible, the theory qualitatively shows the association of a negative $(\partial \ln \epsilon / \partial T)_V$ with a large ϵ and the association of a positive $(\partial \ln \epsilon / \partial T)_V$ with a small ϵ , a situation which is experimentally verified. The relationship of the sign of $(\partial \ln \epsilon / \partial T)_V$ with the magnitude of ϵ

TABLE VI. Constitution of the temperature dependence of the dielectric constants of NaCl, KCl, LiF, and MgO. Results for each material are shown at two temperatures: room temperature and the temperature at which $(\partial \epsilon / \partial T)_V$ is at a maximum. Units are $10^{-4} \text{ } ^\circ\text{K}^{-1}$.

	($^\circ\text{K}$)	$(\partial \ln \epsilon / \partial T)_P = (\partial \ln \epsilon / \partial T)_V - \beta B_T (\partial \ln \epsilon / \partial P)_T$		
NaCl	(295)	3.2	0.3	2.9
	(60)	2.2	1.2	1.0
KCl	(295)	3.0	0.6	2.4
	(40)	2.2	1.8	0.4
LiF	(295)	2.7	-0.7	3.4
	(100)	2.0	1.1	0.9
MgO	(295)	1.0	0.1	0.9
	(150)	0.8	0.4	0.4

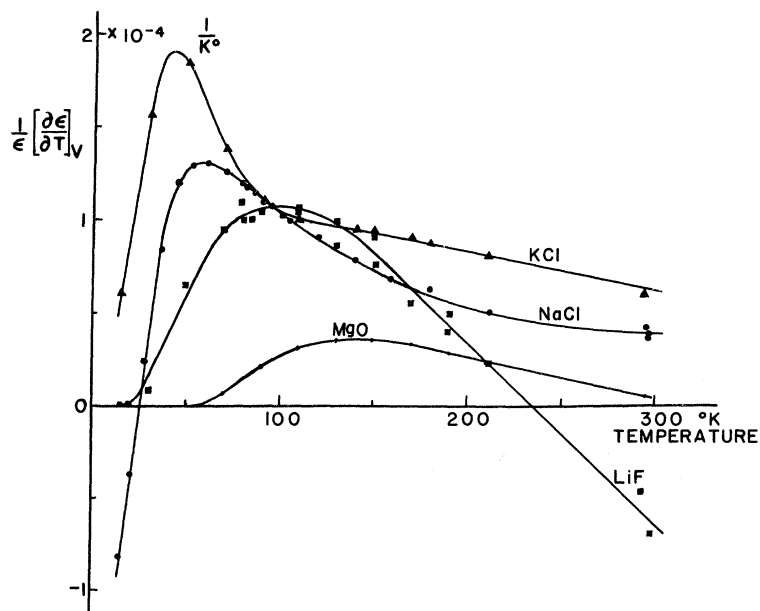


FIG. 3. Fixed-volume temperature dependence of the dielectric constant plotted as a function of temperature. Values are shown for KCl, NaCl, LiF, and MgO. The points represent the values of $(1/\epsilon) (\partial\epsilon/\partial T)_V$ calculated using the results of the individual pressure dependence measurements shown in Fig. 2.

and the crystal structure has been extensively investigated by Havinga and Bosman.^{18,23} Compared to other NaCl-structure-type alkali halides, LiF has a large dielectric constant and Fig. 3 shows it to have a negative $(\partial \ln\epsilon/\partial T)_V$ at the higher temperatures: a result also found by Fontanella, Andeen, and Schuele.¹⁶ In fact for the three alkali halides at the higher temperatures shown in Fig. 3, $(\partial \ln\epsilon/\partial T)_V$ becomes more positive in moving from LiF to NaCl to KCl, the direction of decreasing dielectric constant. Though it is true that MgO has a larger ϵ than any of the three alkali halides considered here and still has a positive $(\partial \ln\epsilon/\partial T)_V$, its doubly charged ions probably do not allow for a simple comparison with the other three compounds.

The fact that the curves in Fig. 3 all reach a maximum value gives plausibility to the idea of two competing effects. Support for the conclusion that Fig. 3 indeed demonstrates lattice dynamical effects is shown in Fig. 4, a graph of $(\partial \ln\epsilon/\partial T)_V$ versus reduced Debye temperature. Here it is seen that for all four compounds the maximum in $(\partial \ln\epsilon/\partial T)_V$ occurs at very nearly the same value of T/Θ_D , about 0.15. It should be emphasized that these four materials cover a large range of Debye temperatures: values used²⁴ were 240, 326, 769, and 1004°K for KCl, NaCl, LiF, and MgO, respectively. This peaking of $(\partial \ln\epsilon/\partial T)_V$ at a common T/Θ_D was also found by Robinson and Hallett¹⁵ in their study of NaCl, KCl, and KBr. They also found a shallow minimum at higher temperatures; we find no evidence for such an effect.

The negative value of $(\partial \ln\epsilon/\partial T)_V$ for NaCl at very low temperatures is very likely due to the same

impurities responsible for the previously considered anomalous effect shown in Fig. 2. One way to reconcile this behavior with permanent dipole impurities is through an order-disorder argument. Fröhlich²⁵ derives an expression for the change in entropy, ΔS , of a dielectric due to the presence of an electric field E ; this expression is (in cgs units)

$$\Delta S = (\partial \epsilon / \partial T)_V E^2 / 8\pi. \quad (3)$$

Equation (3) shows that when $(\partial \epsilon / \partial T)_V$ is negative the application of an electric field leads to a decrease in entropy (increase in order) of the dielectric, the very behavior expected for a dilute solu-

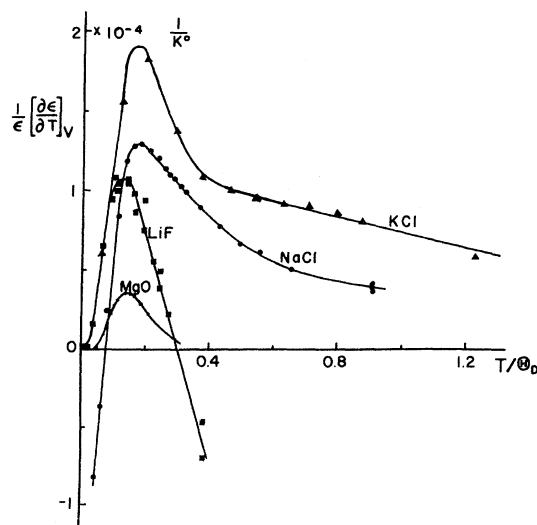


FIG. 4. Same data shown in Fig. 3, plotted as a function of reduced Debye temperature.

tion of freely rotating dipolar impurities or for a solid with dipolar impurities. Also, Eq. (3) plus a direct application of the Third Law of thermodynamics shows that $(\partial\epsilon/\partial T)_V$ must approach zero at absolute zero. The approach of $(\partial\epsilon/\partial T)_V$ to zero is seen in Fig. 3 and Fig. 4 for MgO, KCl, and LiF; and, if measurements had been extended to lower temperatures, the curve for NaCl would also have turned around and approached zero.

C. Havinga's A, B, and C Terms

Havinga²⁶ has developed a straightforward method of breaking up the temperature dependence of ϵ into three physically separate effects. The starting point is the macroscopic Clausius-Mossotti relation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3} \pi \frac{\alpha}{V}, \quad (4)$$

where α is the polarizability of a small but still macroscopic sphere of volume V . Taking derivatives of (4) leads to

$$\frac{1}{(\epsilon - 1)(\epsilon + 2)} \left(\frac{\partial \epsilon}{\partial T} \right)_P = -\frac{\beta}{3} + \frac{\beta}{3} \left(\frac{\partial \ln \alpha}{\partial \ln V} \right)_T + \frac{1}{3} \left(\frac{\partial \ln \alpha}{\partial T} \right)_V = A + B + C. \quad (5)$$

The physical interpretation of these terms is the following: A represents the increase in the number of polarizable particles per unit volume as the temperature is decreased; B represents the decrease in polarizability of a constant number of particles as temperature is decreased (a "crowding" effect due to the shrinking volume); and C is essentially the constant-volume dependence of polarizability on temperature. These terms can be evaluated from dielectric constant temperature-pressure data. A is just minus the linear thermal-expansion coefficient,

$$A + B = -\frac{1}{(\epsilon - 1)(\epsilon + 2)} \beta B_T \left(\frac{\partial \epsilon}{\partial P} \right)_T, \quad (6)$$

and $A + B + C$ is given by Eq. (5). Also by differentiating (4) it is easily seen that

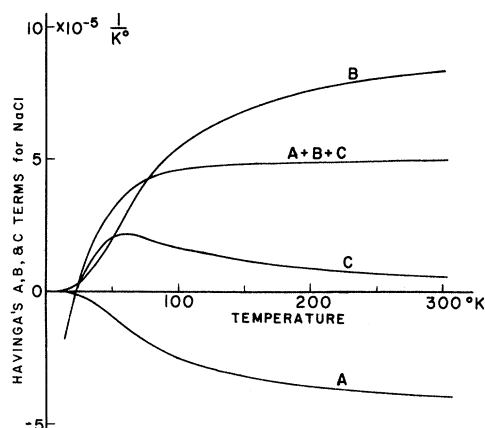


FIG. 5. Constitution of the temperature dependence of the dielectric constant of NaCl according to Havinga's A, B, and C analysis. See text for explanation of the individual curves.

$$C = \frac{1}{(\epsilon - 1)(\epsilon + 2)} \left(\frac{\partial \epsilon}{\partial T} \right)_V. \quad (7)$$

The data presented here allow for the evaluation of these terms over a wide range of temperature and the results of these calculations for NaCl are shown in Fig. 5. Except for the low-temperature impurity behavior seen in Fig. 5 in the C and $(A + B + C)$ terms, the graphs for the other three compounds would be very similar. The two competing thermal-expansion effects, A and B , are seen to get smaller at lower temperatures as the thermal expansions decrease; and the behavior of C is essentially that discussed above for $(\partial \ln \epsilon / \partial T)_V$.

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Impurity-Induced Raman Scattering in SrF₂ and BaF₂[†]

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Measurements have been made of the impurity-induced Raman scattering spectra due to Eu²⁺ impurities substituting for the cations in SrF₂ and BaF₂ single crystals. It is found that the data cannot be fitted to a nearest-neighbor coupling model as has been used previously to fit similar data in some alkali-halide hosts. An electron-phonon coupling model is presented in which purely Coulombic coupling is assumed so that the range of the coupling may be extended beyond the nearest neighbors without introducing new adjustable parameters. As a point-charge model is found insufficient to account for the relative intensities in the regions of acoustic- and optic-phonon scattering, extended charge distributions are assumed for the ionic shells. This treatment gives a qualitative fit to the gross intensity distribution of the observed spectra. However, the approximations used in the model result in some discrepancies between the calculated and observed spectra. It is concluded that the nearest-neighbor coupling model will give an adequate fit to the impurity-induced spectra only in hosts in which all ions in the unit cell vibrate with approximately equal amplitudes in the optic-phonon region.

I. INTRODUCTION

The presence of isolated impurities in a crystal lattice breaks the lattice translational symmetry and therefore also breaks the \vec{k} -vector selection rule for Raman-scattering processes. Numerous experimental and theoretical investigations of such impurity-induced scattering processes^{1,2} have been made both for systems in which the impurity strongly perturbs the vibrations of the host lattice, as well as for substitutional impurities which do not affect the host-lattice eigenfrequencies and eigenvectors. In the latter case, the impurity merely acts as a local optical-polarizability perturbation, and the impurity-induced phonon spectra are related to the density of vibrational states of the host lattice. However, the details of this relationship are a function of the character of the electronic states of the impurity complex and the perturbations of these states by lattice phonons. For example, the ground state and intermediate electronic states which determine the local polarizability of the complex may range from very localized states ($4f^n$ levels of rare-earth ions, for ex-

ample) to energy bands of the host perturbed by the impurity. In the former case, the electron-phonon coupling may have a relatively short range, and a first-order treatment of the impurity-induced scattering in simple crystal lattices is a nearest-neighbor coupling model.¹ In this model the frequency dependence of the scattered intensity reproduces the projected density of phonon states on the nearest-neighbor ions. On the other hand, it is likely that a far more complex model will be required to treat the case of more extended impurity-electron states, and the scattered *intensity* will be less directly related to the phonon density of states, although the *positions* of sharp peaks in the density of states may still be obtained from such experiments.

A recent experimental¹ and theoretical^{1,2} test of the nearest-neighbor coupling model for the Tl⁺ impurity in several alkali-halide lattices led to generally good agreement between the model and the data, except for those crystals in which the cation and anion masses differ appreciably. For KBr: Tl⁺ and KI: Tl⁺, for example, the observed intensity in the optical-mode region, although much