PHYSICAL REVIEW B VOLUME 2, NUMBER 12 15 DECEMBER 1970

Low-Frequency Dielectric Constant of LiF, NaF, NaCl, NaBr, KCl, and KBr by the Method of Substitution*

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(Received 20 July 1970)

The 1000-Hz 300°K dielectric constants of some alkali halides were measured to an accuracy of 0.01% by the method of substitution. Reproducibly different values for various crystals of the same type were obtained which varied beyond the experimental error. The ranges of results for various crystals of each type measured are LiF, 9.0355–9.0360; NaF, 5.0719–5.0722; NaCl, 5.8940–5.8956; NaBr, 6.3957–6.3974; KCl, 4.8112–4.8182; and KBr, 4.8735–4.8762. The spread for each type of crystal is thought to be attributable to random trace impurities. The numbers are discussed in the light of past values.

I. INTRODUCTION

The need for correct values of the static dielectric constant of ionic crystals has increased greatly in recent years. Some of the most interested workers are the shell-model theorists, who ultilize ϵ_s as a fitting parameter to determine the characteristic parameters of their models. They then predict frequency–wave-number relations $\omega(q)$, which are compared with the results from the scattering of thermal neutrons. The reverse process, "best fitting" of the thermal neutron data, also gives results which can be discussed in conjunction with the static dielectric constant.

Further inferences regarding electronic structure and interionic forces can be drawn from values of the Szigeti effective charge[1] and the Szigeti compressibility,[2] each of which requires the value of ϵ_s for its evaluation.

Focus on the static dielectric constant itself has been brought about by first-principles quantum-mechanical calculations such as those of Yamashita[3] and Levin and Offenbacher[4] through their work on LiF. Though Yamashita had few experimental values of ϵ_s to choose from, it must have been disturbing to Levin and Offenbacher to see new values for LiF 3%[5] and 4%[6] lower than that referenced by Yamashita. Still further confusion has been added by a value 9%[7] lower.

Unfortunately, the same sort of scatter exists for most ionic crystals. Several workers have applied themselves to eliminating the discrepancies, but, for the most part, have only succeeded in adding to the confusion.

We believe that we have finally shed some light on existing inconsistencies through an extremely precise and accurate determination of the static dielectric constant of some alkali halides by the method of substitution.[8]

II. THEORY

The method, briefly stated, is as follows. If a fixed-electrode parallel-plate capacitor of area A and plate separation d is used to measure the five capacitances

$$C_1=\epsilon_s^1 A/d \tag{1a}$$

(fluid of static dielectric constant ϵ_s^1),

$$C_2=\epsilon_s^1\epsilon_s^s A/[\epsilon_s^s d+(\epsilon_s^1-\epsilon_s^s)t] \tag{1b}$$

(fluid 1 and sample of thickness t and static dielectric constant ϵ_s^s),

$$C_3=\epsilon_s^2 A/d \tag{1c}$$

(fluid of static dielectric constant ϵ_s^2).

$$C_4=\epsilon_s^2\epsilon_s^s A/[\epsilon_s^s d+(\epsilon_s^2-\epsilon_s^s)t] \tag{1d}$$

(fluid 2 and sample),

$$C_5=A/d \tag{1e}$$

(vacuum), a little aglebra leads to the following equation:

$$\epsilon_s^s=\frac{C_1(1+C_3/C_2-C_3/C_1-C_3/C_4)}{C_5(C_1/C_2-C_3/C_4)}\,. \tag{2}$$

The value of the static dielectric constant of the sample, then, is determined only from ratios of capacitances, the values of which can be known extremely well via three-terminal methods.

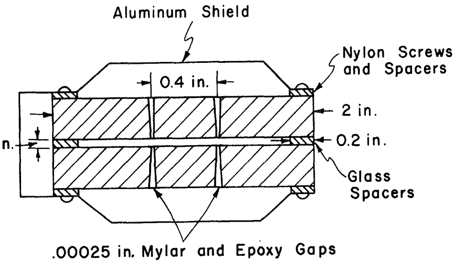

Fig. 1. Cross section of the substitution cell.

III. APPARATUS

A cross section of the substitution cell is shown in Fig. 1. The dimensions shown there ensure a uniform field for 1-in.-diam samples since the condition for the fringing field effects to be insignificant, viz.,

$$\text{effective guard-ring width/gap width}>3, \tag{3}$$

is more than satisfied. The electronics used was basically the General Radio type 1620-A capacitance-measuring assembly. Many details of the equipment are given in our previous aricle.[8] Further aspects of the system are as follows.

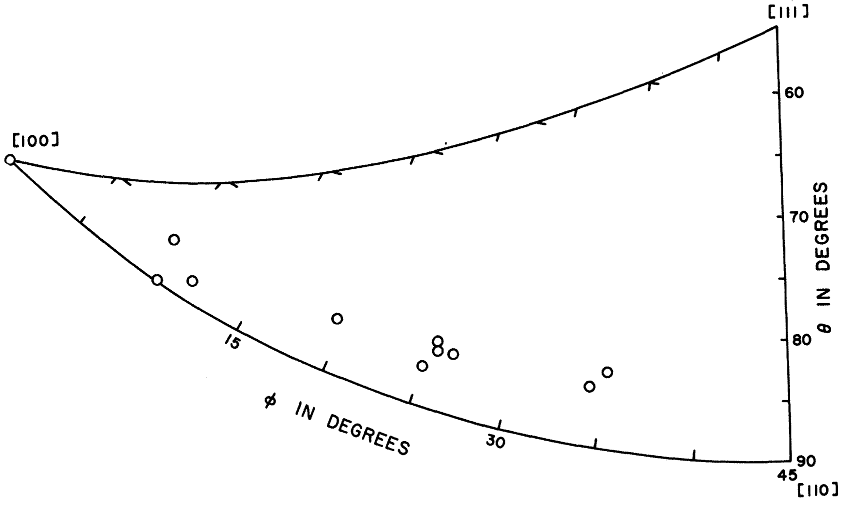

FIG. 2. Directions perpendicular to the faces of the Harshaw NaCl crystals which were purchased in lab packs are plotted on a unit triangle. The corresponding dielectric constants are listed in Table VI.

The General Radio type 1615-A capacitance bridge was rewired such that all operations could be performed with the mode switch in the 3-TERM position. The most important ramifications of this procedure are that both calibration and zero adjustment can be done with the bridge in the same wiring configuration as that used for data taking. The rest of the calibration procedure is as outlined by General Radio in the manual accompanying the bridge. The reference capacitor is a General Radio type 1404-B.

After calibration, the capacitance-selection switches were set to zero, and a null achieved by means of an auxiliary trimming capacitor. The largest zero correction necessary was on the order of 10^{-5} pF. Next, the zero of the total system was investigated. First, the low terminal was connected to the cell in the regular manner with the high side of the substitution cell grounded. No zero offset was observed. The second test was to connect the cell to the bridge in the regular manner and insert a grounded aluminum sheet at the midplane of the cell. The zero was observed first with the ground made at the bridge, then at the substitution cell. The zero remained true in both cases. This extra care was taken with the zero because the final expression for the static dielectric constant, Eq. (2), requires capacitance ratios which would be particularly sensitive to a zero offset.

During the period of modification, the accuracy of the bridge itself was monitored by measuring the ratios of several capacitors, the capacitances of which were on the order of 5 pF, and comparing the values to those obtained using another transformer ratio bridge which was constructed in our laboratory. The results from the two bridges always agreed to within 1 ppm.

Ambiguities related to thermal effects were eliminated because the temperature of the substitution cell was kept constant to within 0.003°C during the course of a run. This was made possible by means of a tiny glass-encapsulated thermistor mounted on the end of a section of Teflon tubing which was used to probe the cell gaps. The resistance was monitored by a precision 27-Hz ac bridge which also was constructed in our laboratory.

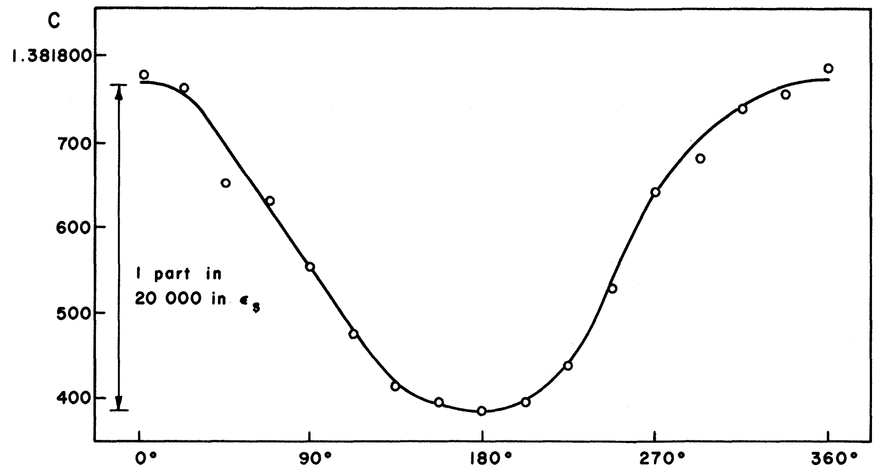

FIG. 3. Capacitance of a Harshaw KBr sample with air as the surrounding medium plotted against the angle of rotation of the sample about a perpendicular to the face of the crystal. The units are pF.

TABLE I. Raw data for sample I of Table VI. The capacitances are in pF. Fluid 1 is Simplex oil, and fluid 2 is castor oil.

	Brass cell		Aluminum cell	
Quantity	Normal	Reverse	Normal	Reverse
C_1	0.890956	0.892490	0.887650	0.898405
	0.890962	0.892496	0.887654	0.898407
C_2	1.966705	1.970022	1.951005	1.974471
(flip)	1.966632	1.970175	1.950866	1.974593
	1.966648	1.970192	1.950878	1.974598
(flip)	1.966764	1.970078	1.950984	1.974465
C_3	1.890956	1.894212	1.884546	1.907371
	1.891252	1.894509	1.884842	1.907671
C_4	2.335950	2.340021	2.325397	2.353601
(flip)	2.335909	2.339905	2.325442	2.353555
	2.336016	2.340017	2.325458	2.353612
(flip)	2.336005	2.340069	2.325486	2.353674
C_5	0.4114849	0.4121925	0.4099567	0.4149261
ϵ_s^8	5.89409	5.89411	5.89404	5.89400

IV. SAMPLES

All samples were obtained in the form of 1-in.-diam disks. Cleaved samples of 0.16-in.-thick LiF, NaF, NaCl, and NaBr were obtained from the Harshaw Chemical Co. in addition to standardized lab packs of nominally 0.225-in.-thick NaCl, KCl, and KBr. Samples of all crystals except NaBr were also obtained from Optovac, Inc. These were about 0.1 in. thick. Similar samples of KCl had been purchased from Optovac about three years prior to this experiment, and were stored in a desiccator during the interim.

Most of the sawn samples were oriented using the back-reflection Laue technique, and the orientations are listed in Tables II–V along with the measured static dielectric constants. The orientations of the lab-pack NaCl crystals are indicated in Fig. 2 on a unit triangle.

The initial step in sample preparation was to cement the samples into steel lapping blocks using phenyl salicylate (salol) and grind them to 0.09 in. using successive grades of number 320, 400, 500, and 600 Carborundum silicon carbide fastcut waterproof paper.

Fine grinding was done on a planetary lapping machine in which five samples per batch were ground using 14.5 μ aluminum oxide oil-based lapping compound. The resultant crystals were 0.062 in. thick.

A satisfactory polish was achieved using a slurry of 5 μ diamond dust and Simplex projector oil on Pellon paper attached to the plates of the planetary lapping machine. The sample thickness was uniform to within 0.0001 in. over the region sampled by the substitution cell.

V. PROCEDURE

The procedure is different from that outlined in our previous paper[8] in that no quantitative air measurements were done. Replacing the air-oil sequence, two liquids only were used: Baker's (U.S.P.) castor oil, which was previously heated to 100°C with silica gel desiccant for several hours, and Simplex projector oil. This was done in order to eliminate problems associated with sample-air interaction due to the hygroscopic nature of the crystals. Extensive testing of the method showed this to be justified.

The approach, then, was to measure the capacitance combinations given in Sec. II using both aluminum and brass cells, each of which contains two separate three-terminal electrode geometries. In addition, the sample was measured in two configurations, the second rotated 180 deg about an axis perpendicular to the face along with a 180 deg rotation about the vertical axis. The 180 deg rotation about the perpendicular to the face was motivated by the fact that the samples are sometimes slightly wedge shaped, and that the diameter of the cavity in the sample insertion tool is in most cases slightly larger than the sample. Thus, it was possible that a different area and thickness of the specimen could have been sampled by the cell for the two oils if only a single measurement were done each time. An order of magnitude for this effect is shown in Fig. 3, where the capacitance for a Harshaw crystal of KBr with air as the surrounding medium is plotted versus the angle of rotation of the crystal about an axis perpendicular to the sample face. It should be kept in mind that an air measurement is an almost direct indication of crystal thickness, and such large effects are not observed with oils. The maximum spread in the dielectric constant that

TABLE II. 1000-Hz 300°K dielectric constants of some (100) NaCl crystals.

Sample	Source and comments	Polishing batch	Measuring group	ϵ_s^8
I	*H*	4	4	5.8943
	Repolished	···	7	5.8945
II	*H*	4	2	5.8952
	Pumped on and heated	4	7	5.8954
III	*H*	4	2	5.8952
	Repolished	···	7	5.8953
IV	*H*	4	2	5.8952
	H	4	4	5.8952
V	*H*	2	1	5.8942
	H	2	4	5.8940
VI	Polished by *H*	···	···	5.8943
VII	0	11	6	5.8956
	Pumped on	11	7	5.8956
VIII	0	7	5	5.8954
IX	0	11	6	5.8952

TABLE III. 1000-Hz 300°K dielectric constants of various crystals of KCl.

Sample	Orientation	Source and comments	Polishing batch	Measuring group	$\epsilon_s{}^a$
I	≈(421)	*H*(old)	0	1	4.8112
II	≈(421)	*H*(old) (0.053 in.)	00	2	4.8113
III	≈(421)	*H*(old)	15	11	4.8113
IV	≈(421)	*H*(new)	19	9	4.8115
V		0(old)	3	3	4.8181
VI		0(old)	3	4	4.8179
VII	(100)	0(old)	3	4	4.8182
VIII	(100)	0(old)	Hand	Reference 8	4.8182
IX	(100)	0(new)	7	5	4.8128
X		0(new)	7	5	4.8127
XI		0(new)	18	9	4.8126

could occur from this effect without rotation is given there to be on the order of one part in 20 000, but it should be noted that two averaged values 180 deg apart reduce this uncertainty drastically. The other 180-deg rotation was for the purpose of averaging any effects due to crystal and electrode surface irregularities.

Still better statistics were obtained by measuring each sample twice during the course of a run. These values were also averaged. The raw data from a typical data run are given in Table I. The results listed in Tables II–VI are an arithmetical average of the four semi-independent values of the static dielectric constant.

VI. RESULTS AND CONCLUSIONS

It is thought that the numbers quoted represent the 1000-Hz 300°K dielectric constant of an individual crystal to better than 0.01%. The ranges of results for various crystals of the types measured are LiF, 9.0355–9.0360; NaF, 5.0719–5.0722; NaCl, 5.8940–5.8956; NaBr, 6.3957–6.3974; KCl, 4.8112–4.8182; and KBr, 4.8735–4.8762, which show spreads of greater than 0.01% in most cases. A detailed analysis of the results shows that impurities are probably responsible for the scatter.

As a test of reproducibility, samples IV and V of Table II were remeasured. The second values agree with the originals to within one part in 30 000. In addition, several checks were made to see if the sample surfaces were contaminated from handling procedures. Samples II of Table II and I of Table IV were heated at 250°C in a vacuum of 10^{-6} Torr for 60 h and sample VII of Table II was pumped on at the same pressure for the same length of time. Samples I and III of Table II, II of Table IV, and NaBr sample I of Table V were repolished for 10 min using the diamond-dust technique mentioned above. In all cases agreement on the order of one part in 20 000 was observed. In addition, the results of two hand-polished crystals, samples VIII of Table III and V of Table IV, fit into the spread of values for their respective types. Also, the dielectric constant of a NaCl crystal polished by Harshaw, sample VI of Table II, was indistinguishable from the rest. Finally, a general investigation of the columns in Tables II–V which enumerate the polishing batches shows no consistent batch dependence.

That there are no sample thickness effects was shown in our previous paper,[8] and the only crystal in this work with a significantly different thickness, the 0.053-in. KCl sample II of Table III confirms this.

TABLE IV. 1000-Hz 300°K dielectric constants of some KBr crystals.

Sample	Orientation	Source and comments	Polishing batch	Measuring group	$\epsilon_s{}^a$
I	≈(432)	*H*	0	1	4.8736
	≈(432)	Pumped on and heated	0	7	4.8739
II	≈(432)	*H*	0	2	4.8737
	≈(432)	Repolished	···	7	4.8741
III	≈(432)	*H*	0	8	4.8739
IV	≈(432)	*H*	5	3	4.8735
V	(100)	*H*	Hand	4	4.8761
VI	(100)	*H*	20	11	4.8755
VII		0	7	5	4.8762
VIII		0	7	5	4.8758
IX	(100)	0	11	6	4.8762

TABLE V. 1000-Hz 300°K dielectric constants of crystals of NaF, LiF, and NaBr.

Type	Sample	Orientation	Source and comments	Polishing batch	Measuring group	$\epsilon_s{}^a$
NaF	I	(100)	*H*	2	1	5.0722
	II	(100)	*H*	2	2	5.0722
	III	(100)	*H*	1	3	5.0720
	IV	(100)	0	8	5	5.0719
	V	(100)	0	8	6	5.0719
LiF	I	(100)	*H*	2	1	9.0357
	II	(100)	*H*	1	3	9.0357
	III	(100)	*H*	1	3	9.0355
	IV	≈(531)	0	8	5	9.0357
	V	≈(531)	0	8	6	9.0360
NaBr	I	(100)	*H*	4	1	6.3971
		(100)	Repolished	···	7	6.3974
	II	(100)	*H*	5	3	6.3957
	III	(100)	*H*	5	3	6.3966

Aberrations due to the loss in the fluids or samples are negligible since the dissipation factors for Simplex oil, castor oil, and all samples were on the order of 20, 200, and 60 ppm, respectively.

In addition, the capacitance was found to be independent of the applied voltage, since when the bridge operating conditions were changed from 30 V, at which value all of the data was taken, to 10 V, no capacitance change was observed.

The most important clues to the spread of static dielectric constants for a given type of crystal are found in Table III, where the results of the "old" and "new" Optovac KCl samples are listed. Note the decrease from 4.818, obtained for the four "old" samples, at least two of which are (100) orientation, to 4.813, obtained for the "new" KCl, at least one of which is (100). This makes accessible the random trace impurity effects on the static dielectric constant. Note that the Harshaw crystals are slightly lower still.

In this light, then, we can discuss Table IV, where two numbers for Harshaw KBr are seen. The (432) orientation crystals show a value of 4.874, while the (100) orientation samples have a value of 4.876. These were probably from different boules, or, at least from different parts of the same boule, since the (432) crystals were sawn while the (100) crystals were cleaved. On the basis of the KCl results, then, this is probably due to impurities rather than an orientation phenomenon. The spread in the static dielectric constant seen in Table II for the (100) Harshaw NaCl crystals further substantiates this conclusion.

Tables II, IV, and V show that the crystals of LiF, NaF, NaCl, and KBr from the two sources are indistinguishable. The results for the crystals of NaBr, which are also listed in Table V show a spread which is on the order of that to be expected from trace impurity effects.

Table VI lists the results for the lab-pack NaCl samples, the orientations of which are indicated in Fig. 2. All crystals show a dielectric constant within one part in 20 000. Thus, there is no anisotropy in the static dielectric constant on the level suggested as a possibility by Robinson and Hollis Hallett.[9]

The most commonly quoted values for the static dielectric constant are listed in Table VII. Let us make some general comments regarding the accuracy of these numbers. First, capacitance values were not reliable prior to the end of the 1950's when three-terminal methods were introduced. Thus, not much confidence can be placed in the early numbers most of which were obtained by mixed-liquid methods.

With the advent of three-terminal techniques, there was a switch to geometrical methods. In the geometrical methods, metal electrodes are attached to the crystal

TABLE VI. 1000-Hz 300°K dielectric constants of Harshaw lab packs of NaCl, the orientations of which are given in Fig. 2.

Sample	Measuring group	$\epsilon_s{}^a$
I	9	5.8941
II	9	5.8943
III	9	5.8942
IV	9	5.8942
V	9	5.8941
VI	10	5.8944
VII	10	5.8944
VIII	10	5.8944
IX	10	5.8944
X	10	5.8943
XI	10	5.8943
XII	10	5.8943

TABLE VII. Some commonly quoted values of the static dielectric constants for the alkali halides measured in this work.

	This work	Lowndes and Martin (Ref. 12)	B. W. Jones (Ref. 7)	Haussuhl (Ref. 6)	Hojendahl[a]
Experimental error	0.01%	0.5%	1%	1%	
Technique	Method of substitution	Geometrical	Geometrical	Mixed liquid	Mixed liquid
Temperature	300°K	290°K	298°K		
NaCl	5.8940–5.8956	5.90	5.72–5.94	5.87	5.62
NaF	5.0719–5.0722	5.08	4.88	5.10	6.0
LiF	9.0354–9.0360	9.00	8.42	8.90	9.27
KBr	4.8735–4.8762	4.90	4.73–4.79	4.89	4.78
KCl	4.8112–4.8182	4.84	4.68–4.77	4.85	4.68
NaBr	6.3957–6.3979	6.27	6.44	6.38	5.99

[a] K. Hojendahl, Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd. **16**, 59 (1938).

by one of several techniques to form a three-terminal capacitor. The first ambiguities are associated with the length measurements necessary to obtain α, the area, and δ, the thickness in order to extract ϵ_s from the governing equation

$$C=\epsilon_s\alpha/\delta. \tag{4}$$

For reasonable size samples (1 in. diam), elimination of the fringing field effects and minimization of total error require that the radius of the guarded electrode be on the order of 0.25 in. and that the thickness be about 0.1 in. It is extremely difficult to obtain a confidence level in these measurements beyond 0.1%, and there is an additional ambiguity associated with α in that it must be ascertained from the outside diameter of the guarded electrode and inside diameter of the guard ring. In addition, it has recently been pointed out[10] that in certain cases electrode-crystal interactions can lead to capacitance enhancement. Additional problems are introduced if there are minute air gaps between the electrodes and the crystal.[11] Thus, there are many pitfalls associated with geometrical methods, and great care must be taken to obtain 0.5% numbers. It appears that Lowndes and Martin[12] have taken that care for their results agree with ours within their experimental uncertainty in each case except for a slight discrepancy in the case of NaBr. The values of Haussuhl[6] also agree with ours within his quoted experimental error, the exception in his work being LiF.

Thus, we believe that we have shed some light on existing data and finally established accurate values for the static dielectric constant of some widely studied ionic crystals. The temperature and pressure variation of the static dielectric constant of these crystals are currently being investigated to a high level of accuracy, and promise to yield further information on intrinsic electronic and associated impurity effects of ionic crystals.

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* Work supported in part by the Atomic Energy Commission.

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