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Anion-cation mirror symmetry in alkali halide ion dynamics

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In an earlier communication by Foldy and Witten, indications were given that "mirror" pairs of alkali halide crystals in which the positive and negative ions of one are replaced, respectively, in the other by the negative and positive ions having the identical isoelectronic structure and nearly the same mass (NaCl-KF, NaBr-RbF, NaI-CsF, and KBr-RbCl) showed very similar crystal phonon properties. The present paper explores the degree to which a more general mirror-symmetry principle, namely that the ion-dynamic properties of mirror alkali halides in both the crystal and melt state are very similar, can be verified by available data. For the crystalline state of the mirror pairs, the dispersion curves along certain symmetry directions and the data available over an extended range of temperatures on specific heats are directly compared, and the infrared reflection data on the RbCl and KBr pair are compared with each other and with that for the pair RbBr and KCl. In addition more than a score of other properties, ion-dynamic and electronic, are analyzed for symmetry by a number of methods specifically developed to give an objective but quantitative measure of this symmetry. The conclusion reached is that indeed ion-dynamic properties of both crystal and melt forms of the alkali halides show quite a high degree of mirror symmetry which is broken in part by the mass differences of homologous ions and in part by the interposition of electronic excitation effects (which do not show this symmetry) into some of the ion-dynamic properties at the higher frequencies. The results also lend credence to the extended symmetry hypothesis proposed by Foldy and Witten to explain certain phonon near degeneracies found in the isobaric crystals but not predicted by the space-group symmetry of these crystals. If mirror symmetry is established it implies near equalities of various other properties of mirror pairs, e.g., viscosity, heat conductivity, thermal diffusivity, self-diffusion coefficients, and x-ray diffraction patterns of melts all as functions of temperature, and corresponding applicable properties of crystals.

I. INTRODUCTION

In a recent communication Foldy and Witten[1] called attention to a pervasive pattern of near degeneracies of Brillouin-zone (BZ) boundary phonons in dispersion data on the isobaric alkali halides: NaF, KCl, RbBr, and CsI. It was also indicated there that this pattern could be understood in terms of a weakly broken "extended" space-group symmetry for these crystals, namely the space-group symmetry of the lattice obtained by regarding the positive and negative ions of these crystals as identical. Thus the extended symmetry of the NaCl structure crystals is that of a simple cubic lattice, while that of CsCl structure crystals is that of the body-centered cubic (bcc) lattice. In turn, this symmetry could be understood as the result of a near invariance of the dynamical equations or the dynamical matrix under Euclidean transformations which exchange anions and cations in these isobaric crystals. It was further noted by Segall[2] that certain near degeneracies of modes not on the BZ boundary could be similarly understood. The evidence for extended symmetry and its possible applications will be presented in detail in another paper.

In Ref. 1 it was also suggested that a natural generalization of the hypothesis underlying extended symmetry could be formulated which relates phonon properties of one (nonisobaric) alkali halide crystal to those of another, its "mirror," obtained from it by replacing anions with their homologous isobaric cations and cations with their homologous isobaric anions, thus giving rise to the mirror

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pairs[3]: NaCl-KF, NaBr-RbF, NaI-CsF, and RbCl-KBr. Some experimental and other evidence was quoted in support of the validity of this generalization, particularly for the pair RbCl-KBr. Our principal concern in this paper will be an attempt to study and assess the experimental evidence for this "mirror" symmetry in alkali halide crystals, its further extension to alkali halide melts and possibly to mixtures. We shall also remark on the practical and theoretical usefulness of the conclusions drawn.

Our present judgment is that there exists substantial evidence for a significant correlation between the properties of these mirror pairs which is particularly strong for the pair RbCl-KBr and that this correlation can possibly be used effectively for simplification in the theory of the phonon properties of these crystals. While the fact that CsCl and CsBr crystallize in the CsCl structure precludes a study of the correlation of their crystalline properties with their mirrors KI and RbI which crystallize in the NaCl structure, when we examine the properties of the melts of these and the other alkali halide salts, we continue to find substantial evidence of this mirror-symmetry property. The problem of formulating completely objective and fairly quantitative appraisals of these symmetries is not a trivial one, and to our knowledge has not been addressed. In the course of this work we have set up a few quantitative measures which are of interest in themselves. We shall present enough detail about the basis of our conclusions to allow the reader to make his own judgment or to propose or test alternative methods of analysis. The final test of the usefulness of what symmetry exists lies in its theoretical and practical usefulness; hence we will make some "target" predictions to allow future experiments to render the last judgment.

In view of some objections and misunderstandings with respect to the thesis developed in Ref. 1, it may be useful to discuss and thus hopefully clarify some of the critical issues involved.

(a) The basis for understanding the near degeneracies in the isobaric alkali halides presented in Ref. 1 is probably common knowledge for many workers in the field of lattice vibrations—a similar basis for understanding corresponding patterns of near degeneracies has been previously recognized in GaAs (Ref. 4) and in beta brass.[5] What *is* surprising is that apparently this pattern of degeneracies in the alkali halides was not recognized in the experimental dispersion relations for the alkali halide crystals obtained from inelastic neutron scattering data during the two decades since 1960, particularly since the "rigid-ion" model of Kellerman[6] (with only nearest-neighbor short-range interactions) predicts an exact extended symmetry of the type postulated in Ref. 1 if only the ionic mass differences are neglected. We may conjecture that the oversight was owing, at least in part, to the discovery of the inadequacy of the rigid-ion model in failing to explain not only the static dielectric behavior of these crystals, but also the early dispersion relation data obtained from neutron scattering. This failure could be attributed to the differences in size, polarizability, and deformability of isobaric anions and cations. The development of various models[7,8] which incorporate these last features into the description of the response of the electronic structure of these crystals to nuclear displacements, such as the polarization dipole models, deformation dipole models, and a variety of shell models, served to circumvent these problems. In these models the extended symmetry is now broken by potential-energy differences as well as mass differences. In consequence, the predicted splittings of these degeneracies are frequently larger than those observed. Nevertheless, even in models[8] which do not use measured dispersion relation data to fix parameters in predicting dispersion curves, the outlines of the pattern of extended-symmetry degeneracies is quite clear even though the predicted splittings may be somewhat exaggerated over those observed. The natural conclusion to be drawn is that this data does indeed suggest that either isobaric anions and cations in the condensed environments of isobaric alkali-halide crystals behave more similarly than what one had come to expect, or that a variety of large contributions to the degeneracy splittings connive to cancel to a substantial degree.

(b) While the evidence of near degeneracies in isobaric alkali halide crystals speaks to the question of the similarity of isobaric anions and cations in the same crystal structure, evidence for mirror symmetry would speak directly to the similarity of the interactions between quite different but homologous ions in mirror environments. While either extended or mirror symmetry could be valid without a corresponding validity of the other, the two types are naturally complementary. They can both be encompassed in a single symmetry hypothesis, namely that the ion dynamics of alkali halide crystals (and melts) is approximately invariant to the replacement of all ions by their isobaric homologues. The fact that of the sixteen alkali halides three crystallize in the CsCl structure rather than the NaCl structure[9] limits a test of crystal mirror symmetry to the four pairs listed earlier, but it is also possible to explore the persistence of the mirror symmetry into the region of the molten state where this limitation does not apply, and possibly further into the domain of crystalline or molten salt mixtures. This carries one considerably further than mirror symmetry in crystals alone, since one now becomes concerned with the potential energy of configurations of ions which cannot be regarded as describable within a harmonic approximation such as is employed in crystals. As we shall see, there is indeed evidence that properties which depend on ionic dynamics in the molten state also display a substantial degree of mirror symmetry. We are, so far, unaware of any previous suggestion as to the possibility of, or an analysis of, evidence for mirror symmetry in either the crystals or melts with one exception.[10]

(c) As we shall see, evaluation of the precise degree and the domain of validity of either extended or mirror symmetry in alkali halides rests in large measure on the availability of both additional data and more accurate data. While we hope that what we present will induce further experiments of the necessary type, we are also well aware that this must be contingent on our success in showing that the concepts in question are practically helpful in terms of providing a coherent picture of phonon-related properties of these condensed materials. We will show that extended symmetries can yield more efficient parametrizations of properties of isobaric alkali halides and suggest pathways to a simpler theoretical description of such of their properties which are approachable in an adiabatic approximation for the response of the electronic structures to nuclear motions. We believe that one of the most important consequences of establishing the reality of mirror symmetry lies in bolstering the hypothesis underlying extended symmetry.

We now briefly summarize the contents of the remainder of this paper. We first discuss the dispersion curves for the four mirror crystal pairs on the symmetry lines Δ and Λ. Originally we intended to include the somewhat incomplete data on the line Σ as well, but decided that since it only confirmed what is already apparent on the lines Δ and Λ, these could be omitted. We follow with discussions of specific-heat data for those of the alkali halides crystals where adequate information is available. In addition we remark on some infrared reflectance data for the mirror pair RbCl and KBr.

We follow with a discussion of particular ion-dynamic properties of alkali halide crystals and melts and present an analysis of the degree of symmetry of these properties for mirror pairs. Included is a discussion of the logic behind the choice of the particular measures of symmetries which were employed, as well as attempts to assess the particular significance of the values obtained and the consistency between different such measures.

We had also intended to follow with an analysis of the Rosenstock sum rule[11] for the dispersion data on the alkali halides since this serves as a more sensitive measure of the importance and similarity of next-nearest-neighbor interactions which are crucial to having a clear understanding of mirror symmetry as well as extended symmetry. However, since the pattern of the sum rule values was more complicated than expected, we have decided to postpone this aspect of the problem to an addendum to this paper.

II. EVIDENCE FOR MIRROR SYMMETRY

The first and perhaps most important properties that we consider are the phonon dispersion relations. These are shown in Figs. 1–4 for $\omega(\vec{q})$ along the (100) and (111) symmetry directions of the fcc Brillouin zone. The "curves" are simply straight line segments connecting data points obtained from inelastic neutron scattering measurements. Particularly striking is the agreement between the dispersion curves for the KBr-RbCl pair for all branches throughout the zone. While the difference between the curves for the other mirror pairs are larger than for the KBr-RbCl pair, they are still considerably smaller than the differences between the curves for arbitrary pairs, so that agreement must still be considered quite satisfactory. This is especially the case for the acoustic branches. Clearly the most significant discrepancies appear in the optic branches. Here two points are relevant. The first is that part of the discrepancies can be accounted for by the differences in the masses of homologous ions, in particular for the light-mass ions. For all the mirror pairs involved aside from the RbCl-KBr pair, the light ions are F and Na and these exhibit the largest fractional mass difference ($\sim 19\%$) between homologous ions. The frequencies at Γ, L, and X can be corrected for this mass difference by assigning the average mass to both ions. One finds that with this correction the discrepancies are reduced

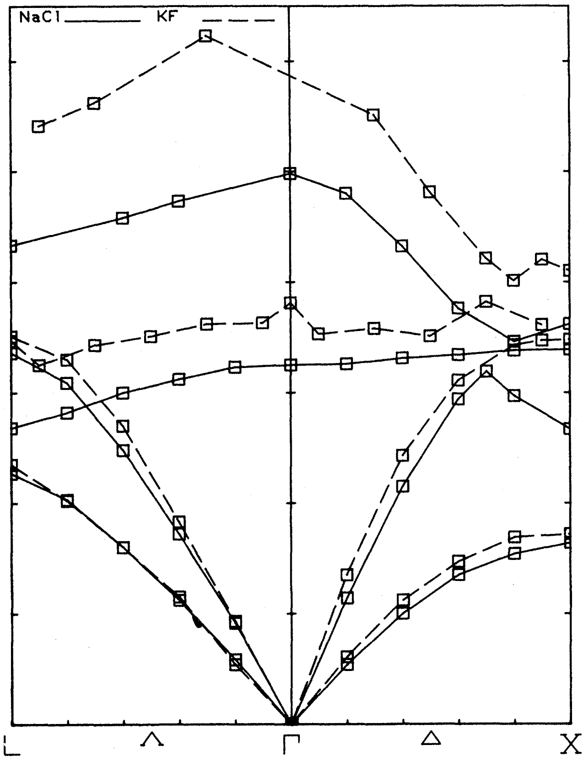

FIG. 1. Phonon dispersion as measured by inelastic neutron scattering along the reciprocal-lattice symmetry axes Λ and Δ for the mirror pair NaCl-KF. Squares represent measured points which are simply connected by straight line segments to guide the eye. The labels on the abscissa are symmetry points and symmetry lines in the Bouckaert-Smoluchowski-Wigner notation. Ordinate scale is in units of 10^{-13} rad/sec, and is identical in Figs. 1–4 so they may be directly compared. Data from Refs. 14 and 15.

by about 30% at Γ and by about 50% at the zone boundaries, indicating a somewhat better symmetry of the potential energy than the direct experimental results suggest.

The second point relates to what we believe is the principal origin of the residual discrepancies in the optical modes. Briefly, in polar materials like the ones of interest here, the optic modes are accompanied by long-range fields, the shielding of which involves the electronic excitation spectra. This is evident, for example, by the occurrence of the high-frequency dielectric constant in the Lyddane-Sachs-Teller[12] relation which concerns itself with the phonons at $\vec{q}\approx 0$. That is to say that for the optic modes—and to some extent the LA and TA modes near the zone boundaries—there is not a complete separation of the vibrations from the excited electronic states. And, as we will see below, the electronic spectra do not exhibit the mirror symmetry.

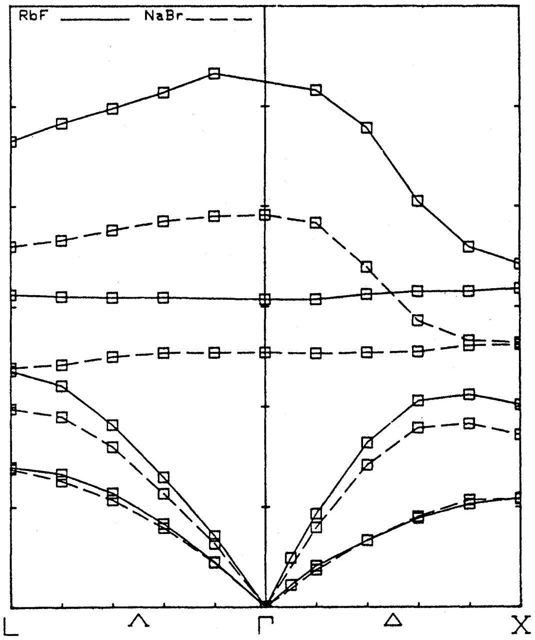

FIG. 2. Same as Fig. 1, but for the mirror pair NaBr-RbF. Data from Refs. 16 and 17.

In Fig. 5 we show the specific heats for all alkali halides for which data[13] in the relatively low temperature range of $0<T\lesssim 50$ K are available. To avoid obscuring the essentials of the figure with too many data points, we have restricted the limited data for KI, NaI, RbBr, and NaF to a single temperature. These points, along with the more extensive data for the other crystals, suffice to indicate the approximate specific-heat values at other

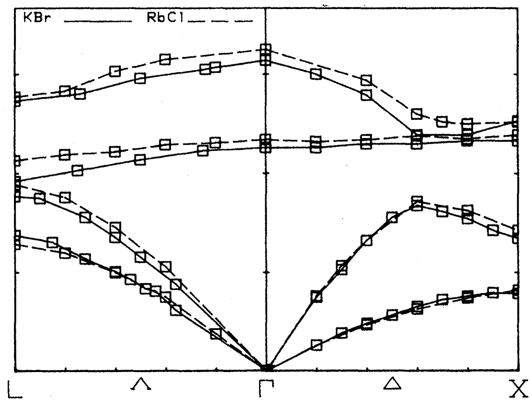

FIG. 3. Same as Fig. 1, but for the mirror pair KBr-RbCl. Data from Refs. 17 and 18.

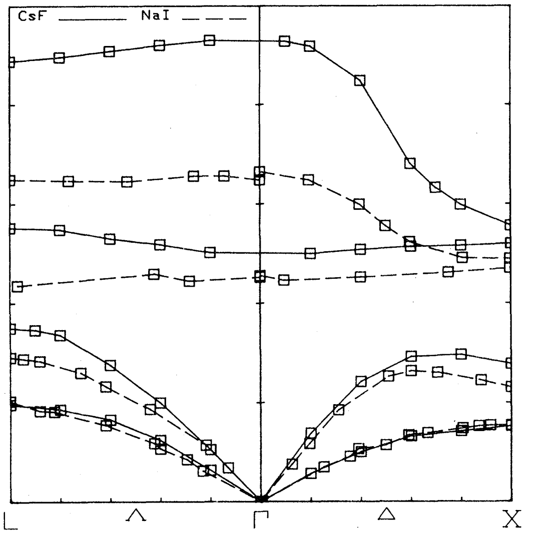

FIG. 4. Same as Fig. 1, but for the mirror pair NaI-CsF. Data from Refs. 18 and 19.

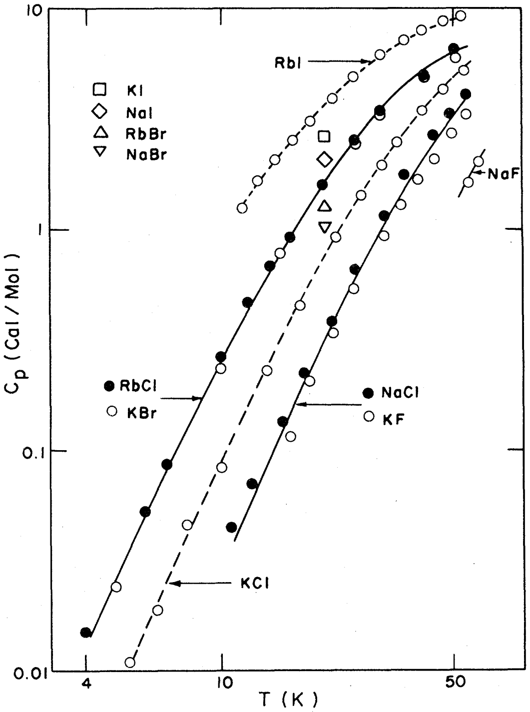

FIG. 5. Low-temperature specific-heat data of alkali halide crystals with NaCl structure. Data from Ref. 13.

temperatures. We note that only two mirror pairs, RbCl and KBr and NaCl and KF, are included in the data set. It is quite clear, however, that the data for each of the mirror pairs lie much closer to a common curve through that data than to curves for the other compounds.

The final graphical presentation of data is Fig. 6, which shows the infrared reflectance spectra[10] for RbBr, RbCl, KCl, and KBr. It is seen that while the spectra for RbBr and KCl are widely separated from each other and the other two, the spectra for the mirror pair RbCl and KBr are remarkably similar.

The data for the remaining properties that we will consider consist of a single number for each compound. For some of these, e.g., $\Theta_D(T=0)$ and the melting temperature, there is strictly a single number while the others in fact vary with external parameters such as the temperature. These temperature variations are small for our purposes and are neglected. In Fig. 7, the data for one property associated with crystalline materials, the static dielectric constant, and for one melt property, the melting temperature, are displayed in the forms of 4×4 arrays. It is clear that these arrays exhibit the mirror symmetry about their principal diagonals. However, this visual assessment is qualitative and perhaps subjective. It is clearly desirable to have more quantitative and objective measures of the degree to which the symmetry is present in the data. To our knowledge, no such measures are available. We therefore have put much effort into developing some quantitative measures for the symmetry which we believe provide objective discrimination. We briefly describe the important considerations in the choice of these.

Ideally, one would like to have a measure of the symmetry of an array which is invariant to all transformations on the array which transform any exactly symmetric array into an exactly symmetric array. It does not seem to be possible to find such a measure except trivial ones, so we must be satisfied with less. It is reasonable, however, to require that the measure should be invariant with respect

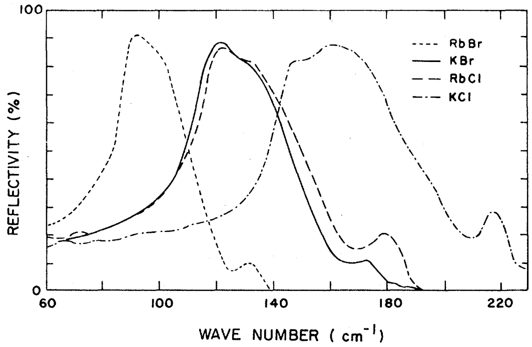

FIG. 6. Infrared reflectivity spectra of RbBr, KBr, RbCl, and KCl. Data from first paper in Ref. 10.

to the units in which a quantity is measured. This will be achieved if the measure is unchanged by multiplication of all elements of an array by any fixed (real) number, and this requirement is fulfilled by having a measure which is homogeneous and of degree zero in the array entries. *This is true of all our symmetry measures.* Since the addition of the same large number to all the elements of an array makes an array "appear" to be more symmetric, it is desirable to have at least one measure which is invariant under this operation as well. The measure which we call FM (figure of merit) has this property and the same is true of the slope of the orthogonal regression line and the standard deviation ratio displayed among the regression line measures in the tables described below.

On the other hand, one can reasonably argue that the zero of the scale is in fact relevant for virtually all these properties, and at least one measure should recognize this. The measure we designate as FMSA does have this property. It also has the property that it is invariant under real orthogonal transformations of the matrix of the array as is also the measure FM (see below). The ratio of the c.m. coordinates among the linear regression measures is another measure which is sensitive to the zero of the scale of the observed property. We can summarize the various symmetry measures we have employed as follows. They fall into two general categories which we call norm schemes and regression schemes.

In the norm schemes the array of available experimental data for a property (with or without some modifications to be described) is converted into a matrix according to the following rules: whenever an experimental value of a property is

	F	Cl	Br	I												
Na	4.73	5.43	5.78	6.62	7.27	5.99	5.11	4.73	4.73	5.43	5.78	6.62	5.99	5.11	7.27	4.73
K	5.11	4.49	4.52	4.66	XX	4.53	4.49	5.43	7.27	XX	XX	XX	4.53	4.49	XX	5.43
Rb	5.99	4.53	4.51	4.55	XX	4.51	4.52	4.55	5.11	4.49	4.52	4.66	4.51	4.52	XX	5.78
Cs	7.27	XX	XX	XX	XX	4.55	4.66	6.62	5.99	4.53	4.51	4.55	4.55	4.66	XX	6.62

ORIGINAL ARRAY ROTATED ARRAY PERMUTED ARRAY ROT. PERM. ARRAY

↓ ↓ ↓ ↓

4.73	5.43	5.78	6.62	7.27	0.00	0.00	0.00	4.73	5.43	5.78	6.62	5.99	5.11	7.27	4.73
5.11	4.49	4.52	0.00	0.00	4.53	4.49	5.43	7.27	0.00	0.00	0.00	4.53	4.49	0.00	5.43
5.99	4.53	4.51	0.00	0.00	4.51	4.52	4.55	5.11	0.00	4.52	4.66	4.51	0.00	0.00	0.00
7.27	0.00	0.00	0.00	0.00	4.55	4.66	6.62	5.99	0.00	4.51	4.55	4.55	4.66	0.00	6.62

ASSOCIATED MATRICES

(a) STATIC CRYSTAL DIELECTRIC CONSTANT ARRAYS AND MATRICES

	F	Cl	Br	I
Na	1265	1074	1023	933
K	1129	1045	1013	958
Rb	1048	988	953	913
Cs	955	918	909	894

(b) ARRAY FOR MELTING POINTS OF ALKALI HALIDES

FIG. 7. Relation of arrays and matrices for alkali halide properties used in the preparation of the symmetry measures of Tables I–III. The upper left array of (a) represents the values of the static dielectric constants of the alkali halide crystals with NaCl structure. The symbol *XX* indicates the value is not available (in this case, since CsCl, CsBr, and CsI crystallize in the CsCl structure). Next to this array on the right is the same array rotated, which is followed in turn by an array formed from the original by one of 24 permutations of the rows, and an array formed by the same permutation followed by rotation. Directly below these four arrays are the associated matrices, formed as described in the text. The array of (b) is the array representing the melting temperatures in K of these sixteen alkali halides. Its associated matrix is identical to the array itself.

not available either because it has not or cannot be measured (instances of the latter are properties of CsCl and CsBr in the NaCl structure), it is represented by zero and so also is the value for its mirror. Thus the arrays in Fig. 7(a) are converted into the matrices below them. For each such matrix the norm is always defined as the square root of the sum of the square of the values of all its elements.

One can calculate from a matrix its symmetric and antisymmetric parts and form the norms of these separately (say, N_S and N_A) and consider the ratio N_S/N_A as a measure of the symmetry. This is in general a large number in the range from fifty to several hundred for the properties of interest. It is much larger than if we dealt with a random array, and from that point of view it would indicate excellent symmetry. However, the entries in general in the array are far from random and hence one must ask about how large a value should be considered good evidence for substantial symmetry? As a measure of this we take $(N_S/N_A)/\langle N_S/N_A \rangle$, where the denominator is the average of the ratio of the symmetric to antisymmetric norms of arrays formed from the original array by the 24 distinct permutations[20] of the rows of the array (or equivalently, its columns). It is this number which is designated by FMSA (figure of merit from symmetric and antisymmetric norms).

FMSA is clearly invariant to unit changes but not to the zero point of the scale. To obtain a measure invariant to the latter we take the ratio where FM is equal to $\langle N_A \rangle/N_A$, where N_A is the antisymmetric norm of the array, and $\langle N_A \rangle$ is again an average of the norms of the antisymmetric matrices formed from the original array by the same 24 permutations of its rows.

A relatively large range of FM values will be encountered below in our survey of relevant data. The question that naturally arises is what does a particular FM value of say, 1.0 or 3.0 mean? To give some answer to this question we have determined the distribution of FM values corresponding to random arrays of numbers uniformly and independently distributed over some range (say 0 to 1.0).[21] The peak of this distribution occurs for an FM$\approx$0.8, and the probability for finding an FM of 2.5 or larger is less than 0.02.

The second group of measures which are employed are based on an analysis of regression. If a value of a property of an alkali halide is plotted as the abscissa and the value of the same property of its "mirror" as ordinate of a point on a Cartesian coordinate system, then for exact symmetry the resultant points for the set of alkali halides will lie on a 45° line through the origin. One can find the straight-line orthogonal regression for the actual points by the condition that the sum of squares of the orthogonal distances from these points to the line is a minimum.[22] Such a line will pass through the center of mass (c.m.) of the points. Thus the c.m. should also be on the 45° line so that one measure of symmetry would simply be the c.m. ratio defined as the ordinate divided by the abscissa of the center of mass. This again is a measure which, while independent of unit size, does depend on the origin of the scale of measurement. The slope of the regression line, however, is independent of this origin as well as the scale unit. Furthermore the closeness of fit of the points to the regression line is another suitable measure of symmetry which can be specified by the ratio of the standard deviation of the points from a line orthogonal to the regression line through the center of mass to the standard deviation from the regression line. (The square of this ratio is simply the ratio of the principal moments of inertia of the points about their c.m.) Note, however, that a large value of this ratio is only a positive indication of symmetry if the regression line slope is close to 45°.

The result of our survey and evaluation of data of relevant properties in the crystalline and melt phases are given in Tables I and II, respectively. The tables, which are nearly self-explanatory are divided roughly into two parts: one giving the measures derived from the norms, the other derived from the regression analysis. The fourth column gives the probability (as a percentage) of finding a random array with an FM equal to or greater than that determined from the data for the given property (i.e., the number listed in the third column). The latter halves of the two major parts of each table give the same measures as the preceding half, but for arrays obtained by rotating the original array by 90° (this is equivalent to calculating the same measures with respect to the minor diagonal). As noted below these provide values to which the measures for the original array can be compared.

A few comments about the tabulated properties are in order. The first is that while all of the listed properties are different, they are not all independent. The properties for which the interdependencies are most significant are the elastic constants, densities, and the sound velocities. The

TABLE I. Quantitative measures of the "mirror symmetry" in data on ion-dynamic properties of the alkali halides: crystal properties.

	Measures derived from norms					Regression line measures					
	Actual array			Rotated array		Actual array			Rotated array		
	FMSA	FM	Prob. %	FMSA	FM	c.m.-coord. Ratio	Slope	Std. dev. Ratio	c.m.-coord. Ratio	Slope	Std. dev. Ratio
Molecular weight	16.3	55.95	<0.01	0.18	0.67	1.01	45.2°	10.75	0.37	−32.7°	4.3
Interionic spacing[a]	2.31	3.28	0.06	0.71	0.94	0.96	51.0°	5.98	0.84	−56.1°	14.6
Density[b]	2.12	2.45	1.8	0.77	0.88	1.11	48.9°	6.93	0.73	−74.5°	5.2
Static dielectric constant[a]	2.99	3.46	0.6	1.48	1.75	1.02	54.1°	8.65	1.14	84.2°	14.7
Reststrahl frequency[c]	3.30	4.11	0.2	0.60	1.03	1.09	53.0°	21.9	1.66	−51.4°	4.8
Debye temperature at $T=0$ K[b]	7.85	18.1	<0.01	0.30	1.04	0.99	47.5°	21.7	2.09	−74.9°	13.9
Cohesive energy[d,e]	3.41	4.38	0.06	0.55	0.71	1.04	48.1°	21.0	1.24	−78.1°	5.1
Elastic constant[b]											
C_{11}	2.12	2.67	3.1	0.91	1.66	1.18	63.1°	78.8	1.48	−64.4°	2.8
C_{12}	2.59	2.92	2.7	0.62	1.27	1.28	54.2°	7.5	2.56	−74.5°	3.6
C_{44}	5.88	11.25	0.04	0.35	1.30	0.94	44.8°	11.2	2.86	−80.4°	19.6
Sound velocity[f]											
trans. (111)	6.16	8.56	0.16	0.56	0.93	1.00	51.0°	15.3	1.46	−77.7°	4.3
long. (111)	10.09	19.08	<0.01	0.38	0.90	0.99	45.2°	18.0	1.66	−77.9°	5.0
trans. (100)	3.04	5.14	0.6	0.39	0.88	0.91	41.8°	11.0	1.98	−73.9°	41.1
long. (100)	6.02	7.95	0.16	0.60	0.94	1.03	50.7°	34.1	1.44	−82.1°	3.8
trans.[g] (110)	4.95	6.33	0.2	0.63	0.95	1.02	53.5°	32.8	1.39	−81.0°	4.0
long. (110)	9.88	16.43	<0.01	0.42	0.91	1.00	46.9°	18.8	1.58	−78.8°	4.4
T at which Debye temperature is minimum[a,h]	7.68	12.25	0.04	0.47	1.06	1.03	48.7°	58.2	2.08	−78.5°	4.8

[a] J. R. Hardy and A. M. Karo, *The Lattice Dynamics and Statics of Alkali Halide Crystals* (Plenum, New York, 1979), p. 162.

[b] A. Konti and Y. P. Varshni, Can. J. Phys. 49, 3115 (1971).

[c] R. P. Lowndes and D. H. Martin, Proc. Soc. London Sect. A 308, 473 (1969).

[d] M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 54.

[e] For all sixteen crystals.

[f] Calculated from elastic constants and densities in footnote b.

[g] The other transverse mode has the same velocity as the (100) transverse mode.

[h] The data are quantities calculated in footnote a.

TABLE II. Quantative measures of the "mirror symmetry" in data on ion-dynamic properties of the alkali halides: melt properties.

	Measures derived from norms					Regression line measures					
	Actual array			Rotated array		Actual array			Rotated array		
	FMSA	FM	Prob. %	FMSA	FM	c.m.-coord. Ratio	Slope	Std. dev. Ratio	c.m.-coord. Ratio	Slope	Std. dev. Ratio
Melting temperature[a]	3.63	4.38	<0.01	0.59	0.71	1.01	54.7°	5.6	1.19	−77.1°	5.9
Boiling temperature[b]	4.19	5.15	<0.01	0.63	0.77	1.00	55.8°	11.6	1.13	−85.5°	5.7
Critical temperature[b]	3.14	3.98	<0.05	0.61	0.77	1.00	55.3°	3.0	1.14	−88.3°	8.5
Average interionic spacing[d]	2.59	3.01	0.2	0.60	0.70	0.95	50.2°	7.9	0.80	−67.4°	3.4
Density at T_m[e,b]	1.71	1.83	2.5	0.82	0.89	1.18	53.4°	4.5	0.71	−79.5°	2.1
Surface tension at T_m[c]	2.19	2.54	0.5	0.62	0.74	1.14	59.4°	8.3	1.56	−84.2°	6.8
Expansivity at T_m[b]	3.97	7.53	<0.01	0.44	0.85	0.99	45.2°	8.0	0.88	76.7°	10.0
Electron conductivity at T_m[b]	3.03	3.83	0.15	0.51	0.71	1.14	55.0°	9.8	3.89	−78.9°	9.4
Heat of fusion[b]	2.11	2.33	0.6	0.72	0.79	0.96	56.2°	2.8	1.23	77.7°	2.3

[a] *Handbook of Chemistry and Physics,* 60th ed., edited by R. C. Weast (The Chemical Rubber Co, Boca-Raton, 1979-80).

[b] G. J. Janz, *Molten Salts Handbook* (Academic, New York, 1967).

[c] G. J. Janz, *Molten Salts,* Vol. 2, NSRDS-NBS 28 (U.S. Govt. Printing Office, Washington D.C., 1969).

[d] Calculated from the molar volumes in footnote a.

[e] T_m denotes the melting temperature.

TABLE III. Quantitative measures of the "mirror symmetry" in properties of alkali halides not directly related to ion dynamics.

Property	Measures derived from norms					Regression line measures					
	Actual array			Rotated array		Actual array			Rotated array		
	FMSA	FM	Prob. %	FMSA	FM	c.m.-coord. Ratio	Slope	Std. dev. Ratio	c.m.-coord. Ratio	Slope	Std. dev. Ratio
Entropy change at T_m[a,g]	0.80	0.83	60	1.27	1.31	0.95	−80.4°	2.3	1.03	17.8°	2.9
High-freq. dielectric const.[b]	1.03	1.06	29	0.92	0.94	0.86	66.7°	1.5	0.83	87.0°	2.6
Sum of ionic polarizability[c]	1.92	2.01	1.4	0.66	0.73	0.74	46.9°	4.6	0.41	−46.3°	1.6
Band gap[d]	1.30	1.36	11	0.83	0.86	1.26	56.1°	3.5	1.38	76.3°	1.9
Threshold energies[d]	1.58	1.68	5.0	0.73	0.78	1.13	38.9°	6.9	1.26	−33.8°	1.2
I(anion)-I(cation)[e,h]	0.84	0.86	55	1.18	1.18	1.65	−89.1°	2.7	1.42	73.0°	3.8
I(cation)-A(anion)[f,h]	0.77	0.84	58	1.47	1.51	0.35	7.6°	2.0	1.66	56.9°	3.0

[a] G. J. Janz, *Molten Salts Handbook* (Academic, New York, 1967).

[b] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[c] S. S. Jawal and T. P. Sharma, J. Phys. Chem. Solids, 34, 509 (1973).

[d] R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. B 11, 5179 (1975).

[e] C. M. Moore, *Atomic Energy Levels,* U.S. N.B.S. Circular No. 467 (U.S. Govt. Printing Office, Washington D.C., 1958).

[f] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), p. 96.

[g] Melting temperature.

[h] I denotes ionization energy and A electron affinity.

sound velocities, of course, are given by simple and well-known functions of the elastic constants and the density. The principal concern here is which sets of quantities should be taken as most significant. The Debye temperature at $T=0$ K is also somewhat related to the same quantities since it can be expressed as the sum of integrals over the solid angle of the inverse third power of the velocities. The second point is that most of the listed properties of the melt, e.g., the expansivity and conductivity, involve terms in the interaction beyond the harmonic approximation. Although one is perhaps most interested in the harmonic term for the crystal, those leading to the dynamical matrix, it is also of interest to consider the possible existence of the symmetry in properties involving anharmonic terms. Note that the values given for the T, for which Θ_D is a minimum, are computed and not observed values.

In regard to the values found for the measures, several points should be noted. For perfectly symmetric arrays the FMSA, and FM, and standard deviation ratio would be infinite while the slope would be 45° and the c.m. coordinate ratio unity. An example of a data array which clearly exhibits a very high degree of symmetry is provided by the molecular weights, the first entry in Table I. (The molecular weights of members of a pair differ by less than 1.5%, while molecular weights range from 42 to 260.) A perusal of the tables will show the reader that the quality of the various measures are generally rather consistent. This is certainly the case with the FMSA and FM whose trends parallel each other to a fairly high degree, as these measures vary over a range roughly from 2.0 to 20. This consistency of these quite different measures is, of course, gratifying. Some idea of the significance of the FM value is afforded by the probability that it is exceeded for random arrays (the fourth column) which for most properties is below 1% and has a maximum value of 3.1%. The significance of even these values may also be questioned since they involve the comparison of totally random arrays with actual data arrays which have some "built in" trends as a result of the fact that the rows and columns of the array are ordered by the ordering of alkalis and halides in the Periodic Table. A completely independent means of assessing the significance of the measures is provided by examining the same measures for the rotated arrays. It is seen that the quality of the measures of the symmetry drop substantially and, in fact, generally *approach* the peak of the probability density for the random arrays. The only measures which do not always show unfavorable values are the c.m.-coordinates and standard deviation ratios. But even in those cases, the slopes of regression lines deviate so markedly from the ideal value that these results of the regression line test cannot be considered favorable.

To provide still another "test," we analyzed a number of properties which we had no reason to expect would show mirror symmetry in the same manner as those listed in Tables I and II. The results of that analysis are given in Table III. Except for the first entry in the table, the entropy change at melting, all the properties relate to the electronic excitation spectra of the solids or the atoms. The results show that the quality of all measures of those properties is distinctly poorer than of those in the preceding tables. Another point worth noting is that the quality of the symmetry measures is not particularly poorer for the rotated arrays than those for unrotated arrays, contrary to the behavior in Tables I and II.

Before drawing any conclusions from the information presented in the figures and tables, it would be reasonable to indicate how this data has been selected since this clearly can bias the results. The principal criterion was, of course, the availability of sufficiently extensive data about an alkali halide property to make the analysis by the methods described feasible. We did attempt to track down data on those properties which we felt were clearly relevant in establishing or refuting our thesis on the symmetry we were investigating. Certain compilations listed in the references to the tables were particularly helpful. In some instances, there existed two or more sets of data which were clearly so closely related that use of all of it would be redundant. Here we used the form of the data which we felt was most relevant (such as interionic spacing rather than molar volumes for melts). As noted earlier, we have sometimes included data which are not independent, e.g., sound velocities, elastic constants, and densities.

There are some inadvertant omissions. This includes particularly the data on Born-model repulsive interactions as determined from ultrasonic data by Smith and Cain[23] which appears to support our symmetry thesis, as do some results of Roberts and Smith[24] on the Born model of sodium and potassium halides, while some work of Smith and Cain[25] on temperature derivatives of elastic constants appears either hostile or ambivalent to our thesis. The results of Fumi and Tosi[26] on crystal ionic radii also lend support to our thesis. The work quoted in Ref. 10 contains information which also tends to support mirror symmetry in certain mixed crystals.

It is likely that we may have missed much more relevant information, favorable and unfavorable, through ignorance of its availability, and we would welcome the publication of it by others who may have access to such knowledge so as to assist in understanding the validity and the limits of this symmetry.

III. CONCLUSIONS

It is our belief that the clear conclusion can be reached from the data summarized and analyzed in the preceding section that mirror symmetry is indeed manifested to a fairly high degree in the ground electronic states of alkali halides, both as crystals and melts, and that this lends support to the hypothesis of extended symmetry of the isobaric crystals. If this is indeed the case, we may draw a number of conclusions which (if not already supported or refuted by data of which we are not aware) could be used to further test this symmetry hypothesis. We indicate some of these here:

(1) Close similarities of the infrared reflectance properties of the melts of mirror alkali halides, as well as of their crystals, is to be expected as functions of both frequency and temperature.

(2) In the case of mirror melts, if the electrical conductivity and dielectric constant should become complex and a function of frequency up to the microwave region, we would expect their behavior to be similar as functions of frequency as well as of temperature.

(3) Such transport properties as viscosity, heat conductivity, thermal diffusivity, and self-diffusion would be expected to be similar as functions of temperature in mirror melts, as well as in mirror crystals where applicable.

(4) X-ray diffraction data on the melts of mirror alkali halides should show strong similarities with respect to both radial structure and intensity of the diffraction rings at corresponding temperatures and x-ray wavelengths. The ionic radial distribution functions obtained by neutron diffraction should also be similar.

(5) We would expect the same mirror symmetry to hold for melts formed from mixtures of alkali halides and homologous melts formed from their mirrors, as well as for crystalline alloys and their mirror alloys. There already exists evidence for the latter in Ref. 10 with respect to infrared reflectivity and in some further work[27] on infrared absorption.

(6) On a lighter note, we may expect that at some future time it may be possible to study further mirror pairs including the francium halides and alkali astitides, and find them also exhibiting mirror symmetry in their properties.

If in fact our thesis is accepted as correct, it poses an interesting theoretical question as to how to justify mirror symmetry and extended symmetry from first principles. In Ref. 1, the existence of a second set of near degeneracies at the point X for all alkali halides with NaCl structure was pointed out, and a possible dynamical reason for their occurrence suggested, but further understanding is also clearly needed here.

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[1] L. L. Foldy and T. A. Witten, Jr., Solid State Commun. 37, 709 (1981).

[2] Reference 1, footnote 7.

[3] The further pairs CsCl-KI and CsBr-RbI are omitted since CsCl and CsBr crystallize in the CsCl structure while their homologues KI and RbI have the NaCl structure. While this may appear to violate the symmetry principle we enunciate later, we do not regard this as serious since the energy difference between the two crystalline forms is known to be small.

[4] G. Dolling and J. L. T. Waugh, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 19.

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[18] A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. 131, 1025 (1963); $\omega(\vec{q})$ of NaI and KBr.

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[20] It would be possible to consider all possible permutations of the elements of the array, but the additional computational effort required did not appear to be justified in terms of leading to a better symmetry measure.

[21] The same was not done for FMSA, since in this case the ratio of the width of the interval over which the random numbers were distributed to the location of the center of interval would have to be separately specified for each property.

[22] See, for example, H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, 1946), p. 309. The usual linear regression is not suitable for our purposes since it is not symmetric with respect to exchange of ordinate and abscissa. All points were assessed equal weight.

[23] C. S. Smith and L. S. Cain, J. Phys. Chem. Solids 36, 205 (1975). Although this data on Born-model repulsive interactions could not be included in Table I, we did calculate our symmetry measures for the quantity π as defined in this reference: $\pi = -r^2 W_R'' / r W_R'$, where W_R is the lattice energy excepting the Coulomb energy. The results are FM=3.25 and FMSA=1.91 for the original array, and FM=0.86 and FMSA=0.53 for the rotated array. For the regression measures, the original array has c.m. coordinates equal to 1.04, regression line slope equal to 52.7°, and the standard deviation ratio equal to 14.1, while for the rotated array, the numbers are 0.87, −61°, and 1.71, respectively.

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