PHYSICAL REVIEW B VOLUME 29, NUMBER 4 15 FEBRUARY 1984

Anion-cation mirror symmetry in alkali halide ion dynamics. II

L. L. Foldy and B. Segall
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106
(Received 21 July 1983)

This Brief Report supplements a previous survey and analysis of data relating to the ion-dynamic properties of alkali halide crystals and melts which indicated that mirror symmetry is manifested to a fairly high degree in these materials. The further evidence here presented adds support to the symmetry hypothesis, particularly for the mixed (alloy) pairs related by $K^+ \leftrightarrows Cl^-$, $Rb^+ \leftrightarrows Br^-$. The conjecture that symmetry breaking results largely from electronic excitation (as well as ion-mass difference) is briefly examined.

A series of recent papers[1-3] have dealt with some evidence for and predictions from certain weakly broken symmetries associated with the alkali halides (excepting the lithium halides). In their broadest form these symmetry principles may be encompassed in the statement that the ion dynamics of alkali halides (pure or mixed) in condensed states (crystalline and molten) is approximately invariant with respect to the replacement of the positive alkali ions with their homologous (isoelectronic and approximately isobaric) negative halide ions, and the negative ions by their homologous positive ions. In crystals composed of an alkali ion and its homologous halide ion (NaF, KCl, RbBr, and CsI) this symmetry is called *extended symmetry* of the crystal. In cases where the symmetry leads to near equality of ion-dynamical properties of a crystalline or a molten phase with its mirror phase different in composition from the original we refer to it as *mirror symmetry.* The present paper represents an addendum to Ref. 2 which examined much of the available evidence bearing on the validity of this latter symmetry. The conclusion from Ref. 2 was that available evidence generally supported the mirror symmetry hypothesis. We here examine some additional evidence relevant to exploring the limits of validity of mirror symmetry and the scope of the phenomena it encompasses. For nomenclature and explanation of the concepts involved (particularly the symmetry measures) a reading of Ref. 2 is necessary. We follow with our additions.

(1) In the work of Angress, Chambers, Gledhill, and Smith[4] referred to in MS I, attention was called to the near equality of the infrared reflectance of the mirror crystals KBr and RbCl. Figures 4 and 5 of that reference show also the reflectance properties of random concentrated alloys of crystals with the compositions

$$RbCl_xBr_{1-x} \leftrightarrow K_xRb_{1-x}Br$$

for the common values $x=0.2$, 0.5, and 0.75. These alloys are also mirrors of each other. To illustrate better that the reflectivities have very similar magnitudes and frequency dependence, we have replotted the results in our Fig. 1 which directly compares the reflectivities of these mirror alloy pairs. The curves for different composition parameters x are displaced vertically to disentangle them.

Figures 2 and 3 of Ref. 4 give similar curves for the alloys KCl_xBr_{1-x} and $K_xRb_{1-x}Cl$ but, unfortunately, there are no common values of x for the two sets of measurements. Interpolation between the values given suggests agreement with mirror symmetry to the same order of accuracy as in our Fig. 1. The authors of Ref. 4 have noted the mirror symmetry in this special context as was remarked in MS I, and this is the earliest reference to mirror symmetry of which we are aware.

Recently Beg and Kobbelt[5] have measured phonon dispersion relations by coherent inelastic neutron scattering in the two mixed crystals $K_{0.5}Rb_{0.5}Cl$ and $KBr_{0.5}Cl_{0.5}$, which again constitute a mirror pair. They find what is generally a doubly peaked distribution of frequencies for each $\vec{q}$. We have replotted their mean frequency for each $\vec{q}$ along Δ and Λ in Fig. 2 for both crystals. One sees that the dispersion relations are virtually identical for the TA, LA, and TO branches (considering the experimental errors) and agree to about 5% for the LO branch. The same behavior is observed along Σ though the data here are somewhat sparse. Clearly, mirror symmetry appears to be a remarkably good symmetry in mixed crystals of the $K_xRb_{1-x}Cl_yBr_{1-y}$ class from presently available evidence. It would be of particular interest to observe the analog of extended symmetry in the

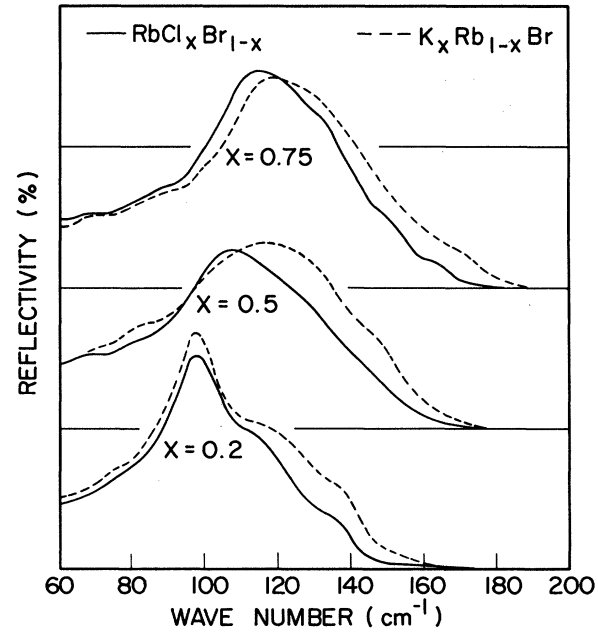

FIG. 1. Infrared reflectance of the mirror crystals $RbCl_xBr_{1-x}$ and $K_xRb_{1-x}Br$ compared for several values of x. The zero reflectance ordinate for each pair is the horizontal line which it approaches at high wave number. The reflectivity differences between adjacent horizontal lines is 50%. Data from Angress *et al.* (Ref. 4).

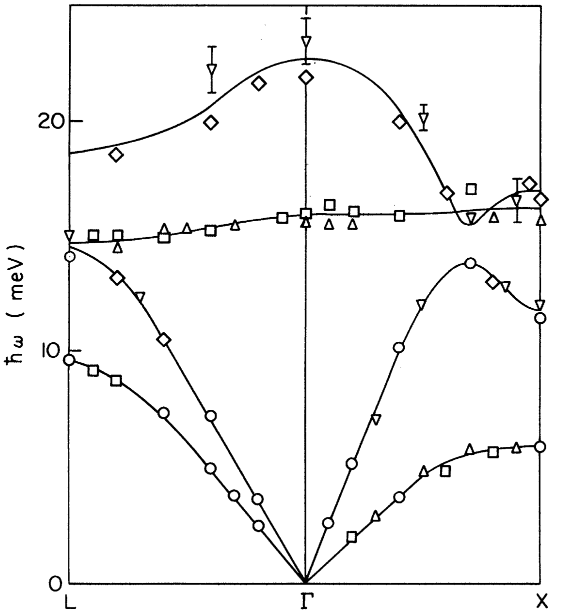

FIG. 2. Dispersion data from Beg and Kobbelt (Ref. 5) for the mirror crystals $KCl_{0.5}Br_{0.5}$ [$\Delta(T), \nabla(L)$] and $K_{0.5}Rb_{0.5}Cl$ [$\square(T), \Diamond(L)$] along Λ and Δ axes. Where two point symbols for different crystals overlap, a ○ is used. Curves are drawn by eye to indicate an approximate best fit to the data on the same branches of both crystals. Error bars are drawn on the symbols for the LO modes of $KCl_{0.5}Br_{0.5}$. Errors are smaller for other points.

self-mirror mixed crystal $K_{0.5}Rb_{0.5}Cl_{0.5}Br_{0.5}$.

(2) We briefly comment here on studies of the same systems as in (1) but in the dilute alloy limit [i.e., $x \ll 1$ or $(1-x) \ll 1$]. The work is that of Gledhill, Syms, and Angress[6] on the infrared absorption spectra of $RbCl_{0.99}Br_{0.01}$ and its mirror $K_{0.99}Rb_{0.01}Br$, as well as $KBr_{0.99}Cl_{0.01}$ and its *near* mirror $Rb_{0.98}K_{0.02}Cl$. The impurities in these cases lead to new modes whose frequencies lie in the gap between the acoustic- and optical-mode frequencies of the crystals RbCl and KBr, respectively. In turn, these give rise to a prominent new far-infrared absorption peak lying in the region of this gap. In the case of the first pair of alloy crystals the peaks lie at 102–103 cm^{-1} in the first crystal and at 99–100 cm^{-1} in the second, while for the second pair they lie at 93–95 cm^{-1} is the first crystal and at 97–100 cm^{-1} in the second. Mirror symmetry for these two pairs of mirror crystals is thus confirmed to about 3% as far as the frequencies of absorption peaks is concerned. The data of Gledhill *et al.* give the absorption in arbitrary units so it is not possible to compare the actual absorptivities as well; from mirror symmetry we would expect these also to be nearly equal for the members of the first mirror pair and to differ by a factor of approximately 2 for the second pair. It is also relevant that the widths of the absorption peaks are similar for the members of each mirror pair.

(3) In a pair of classic papers[7,8] in 1964, Fumi and Tosi determined new values of the radii of alkali and halide ions in the NaCl structure crystals for all the alkali halides (including CsCl, CsBr, and CsI, by using the work of Schultz). These radii were found to be nearly but not precisely equal for the same ions in different crystals, the differences ranging from 1% to 5% except for F^- where they range up to slightly less than 10%. While reference should be made to these papers for details of the process of radius determination, we shall simply use the results quoted in Table 3 of Ref. 8 to calculate the same measures of mirror symmetry as were employed in MS I. For the 16 crystals, we get two sets of measures: one set using the radius of the less massive ion in each crystal and the other using the radius of the more massive ion in each crystal. The first is referred to as TF (Tosi-Fumi) ionic radii I and the other as TF ionic radii II in our Table I. As one observes, the symmetry measures are in both cases as supportive of the mirror symmetry hypothesis as the results for other properties quoted in Table I of MS I.[9]

Mention should also be made, in this connection, of the work of Abramo *et al.*[10] on the prediction of partial structure factors for the alkali halide *melts,* using the mean spherical approximation theory of the liquid state[11] in combination with parametrizations of ionic interactions based on the results of Fumi and Tosi[7,8] obtained from their analysis of crystal data as described above. The predictions are compared with available x-ray data[12] and neutron-diffraction data[13] on the melts, but these data are not yet adequate to provide a *test* of mirror symmetry though they are consistent with mirror symmetry.

It is also worth mentioning that the prediction of near

TABLE I. Quantitative measures of mirror symmetry in ion dynamics of alkali halides. (For definition of symmetry measures see Ref. 2.)

	Norm measures		Regression line measures		
	FMSA	FM	c.m. coordinates ratio	Slope	Standard deviation ratio
TF ionic radii I[a]	3.30	4.39	1.04	54.0°	27.4
TF ionic radii II[a]	1.73	1.83	0.91	39.4°	14.8
Smith-Cain parameters[b]					
π	1.91	3.25	1.04	52.7°	14.1
A	5.72	9.25	1.04	52.6°	150.0
B	5.48	8.71	1.02	50.0°	90.5

[a] Data from Table 3 of Ref. 8.

[b] Data from Ref. 17.

equality of partial structure factors (or radial distribution functions) for mirror alkali halide melts should hold for the crystals as well. In particular, for *isobaric* crystals with extended symmetry one should expect that x-ray powder diffraction patterns of these would show only the lines characteristic of a simple cubic (sc) crystal lattice for those crystals which have the NaCl structure and those characteristic of a bcc lattice for those having the CsCl structure. That this is, in fact, the experimental situation in the isobaric alkali halides, in the sense that lines expected in NaCl (CsCl) structure which should not be present in sc (bcc) are very weak, has been known since the 1920s.[14,15] This is a significant but not very sensitive test of extended symmetry.

In the case of nonisobaric mirror crystals one might expect that the intensities of corresponding x-ray powder diffraction lines should be the same. The data here are rather confused as shown by the National Bureau of Standards data by Swanson *et al.*[15] on relative intensities of various lines. While the correlation between intensities for mirror pairs of crystals is quite fair, it is sometimes not as good as that between nonmirror pairs (see KF vs NaCl as against KF vs RbCl). This situation could easily change if one were comparing absolute intensities. So far we have not been able to find appropriate data of this kind, and thus it would be premature to draw a definite conclusion relative to mirror symmetry from this consideration at this time.

(4) We turn now to the work of Roberts and Smith[16] and of Smith and Cain[17] in which information concerning the Born-model repulsive interactions is obtained from ultrasonic measurements of the temperature derivative of the isothermal bulk moduli of the alkali halides in their crystal form for all but the iodides. The experimental results are summarized in terms of the parameter

$$\pi = -r(W_R''/W_R')_{r=r_0} \ ,$$

where W_R is defined to be the lattice energy excepting the Coulomb energy. Considering W_R as written in the power-law form $A(r_0/r)^n$ or in the exponential form, $D\exp\{-(d_0/\rho)[(r/r_0)-1]\}$, π is directly $n+1$ or d_0/ρ in the two cases, whence knowledge of the bulk modulus gives one the coefficients A and D as well. We may take the purely experimental quantity π as well as the derived parameters A and D and calculate our symmetry measures of Ref. 1 for them. These are presented in Table I and show ample support for the mirror symmetry hypothesis.

(5) While in MS I we had expressed the hope that use of the Rosenstock sum rule[18] would allow us to make a more critical analysis of next-nearest-neighbor interactions, we were disappointed in this expectation. Such an analysis provides us with no more information than can already be gleaned from a study of the experimental dispersion relations as illustrated in Figs. 1–4 of MS I. Clearly, one would expect to find that $\sum_j \omega_j^2(\vec{q})$ would be nearly identical as functions of $\vec{q}$ in the pair KBr-RbCl and quite unequal for the other mirror pairs—and for these last, better agreement would be found in the neighborhood of the point X than in other regions of $\vec{q}$ space. If, as is suggested in MS I, the discrepancies in the optical dispersion curves for these are owing to the effect of electronic excitation on the optical branches (which dominate the sums), the same explanation would apply to the discrepancies in the Rosenstock sums.

The above considerations further buttress the hypothesis of mirror symmetry in condensed states of alkali halides, and particularly so for those mirror pairs obtained one from the other by the ion exchange: $K^+ \rightleftarrows \mathrm{Cl}^-$, $\mathrm{Rb}^+ \rightleftarrows \mathrm{Br}^-$. At the same time, the available evidence seems to make it clear that mirror symmetry in the mirror pairs (perhaps, excepting RbCl-KBr) is a more strongly broken symmetry in the nonisobaric crystals, and particularly for the optical modes of these, than is extended symmetry in the isobars. It is, of course, important to understand the origins of the symmetry breaking if the symmetry itself is to be understood.

We therefore further note that the observed pattern in the strength of symmetry breaking related above can be understood if we assume that (apart from the mass differences of homologous ions) the important element in the symmetry breaking is the coupling of electronic excitation to optical modes of the lattice. As a measure of this coupling we can take the high-frequency dielectric constant[19] ϵ_∞, or better $\epsilon_\infty - 1$, the value of which generally differs appreciably for the two members of each mirror pair. Since an isobar is "self-mirror," the difference for it vanishes trivially. The fractional differences of $\epsilon_\infty - 1$ for the four pairs are

NaCl-KF: 0.45, NaI-CsF: 0.50 ,
NaBr-RbF: 0.49, RbCl-KBr: 0.12 .

Thus one would anticipate the breaking of mirror symmetry owing to electron excitation would be considerably smaller in RbCl vs KBr than in the other mirror pairs, as is observed.

ACKNOWLEDGMENT

Support by the National Science Foundation under Grant No. PHY-80-10695 is gratefully acknowledged.

---

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

[2] L. L. Foldy and B. Segall, Phys. Rev. B 25, 1260 (1982), hereinafter referred to as MS I.

[3] B. Segall and L. L. Foldy, Bull. Am. Phys. Soc. 27, 274 (1982); Solid State Commun. 47, 593 (1983). See also M. Mostoller, Phys. Rev. B 26, 4543 (1982).

[4] J. E. Angress, W. E. Chambers, G. A. Gledhill, and W. Smith, J. Phys. C 9, 3717 (1976).

[5] M. M. Beg and M. Kobbelt, Phys. Rev. B 26, 1893 (1982).

[6] G. A. Gledhill, M. Syms, and J. F. Angress, Infrared Phys. 18, 915 (1978).

[7] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids 25, 31 (1964).

[8] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids 25, 45 (1964).

[9] The probabilities associated with obtaining FM values exceeding various limits as given in Tables I, II, and III (fourth column) of MS I are not particularly meaningful for FM exceeding 2.0 because of small sample sizes. A better guide is the following: Prob(FM > 3) < 1%, Prob(FM > 2.5) < 2%, Prob(FM > 2) < 5%.

[10] M. C. Abramo, C. Caccamo, G. Pizzimenti, M. Parrinello, and M. P. Tosi, J. Chem. Phys. 68, 2889 (1978).

[11] E. Waisman and J. L. Lebowitz, J. Chem. Phys. 56, 3086 (1972).

[12] J. Zarzycki, J. Phys. Radium A18, 65 (1957); A19, 13 (1958); B. D. Antonov, Zh. Strukt. Khim. 16, 501 (1975).

[13] J. Y. Derrien and J. Dupuy, J. Phys. (Paris) 36, 191 (1975); F. G. Edwards, J. E. Enderby, R. A. Rowe, and D. I. Page, J. Phys. C 8, 3483 (1975); E. W. Mitchell, P. F. J. Poncet, and R. J. Stewart, Philos. Mag. 34, 721 (1976).

[14] W. P. Davey, *A Study of Crystal Structure and its Applications* (McGraw-Hill, New York, 1934), pp. 138–141.

[15] Natl. Bur. Stand. (U.S.), Circ. 539 (1953–1960), Vols. 1–10; Natl. Bur. Stand. (U.S.), Monogr. 25 (1964–1982), Secs. 1–12.

[16] R. W. Roberts and C. S. Smith, J. Phys. Chem. Solids 31, 619 (1970).

[17] C. S. Smith and L. S. Cain, J. Phys. Chem. Solids 36, 205 (1975).

[18] H. R. Rosenstock, in *Lattice Dynamics,* edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 19.

[19] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), p. 553.