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Review
Physical properties of mixed crystals of alkali halides

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The physical properties of mixed crystals of alkali halides are reviewed. The properties considered are experimentally determined quantities like the lattice constants, the compressibility, the elastic constants, thermal expansion, specific heats, Debye–Waller factors, dielectric constant, refractive index, IR spectra and Raman spectra and also some calculated solid-state parameters like Debye temperatures and lattice energies. A critical analysis of composition dependence shows four groups designated as follows: Type A, properties which vary linearly with composition; Type B, properties which vary slightly non-linearly with composition; Type C, properties which depend highly non-linearly on composition with the values for mixed crystals exceeding the values for end members; and Type D, properties which are peculiar to the mixed crystals and are not shown by the parent crystals. Most of the physical properties belong to Types A or B. Variation of Type C is shown only by properties affected by differences in ion size like the Debye–Waller factor and the microhardness. Properties which are symmetry-dependent like the first-order Raman spectrum and the IR spectra are of Type D. Attention is drawn to areas where further work is needed.

Nomenclature

a	Lattice constant
A	Madelung constant
α	Coefficient of expansion
b	Repulsion constant
B	Debye–Waller factor
C_{11}, C_{12}, C_{44}	Elastic constants of a cubic crystal
d	Density
δ	Percentage difference in lattice constants
e	Electron charge
ε	Dielectric constant
H	Heat of formation
K	Bulk modulus
ψ	Compressibility
μ	Reduced mass
r	Interionic spacing
R	Refractive index
T	Temperature
Θ	Debye temperature
U	Lattice energy
v	Volume per molecule
V	Molar volume
λ	Wavelength

The composition of mixed crystals is given in molar fraction, x. Thus the mixed crystal $KCl_xBr_{(1-x)}$ contains x mole fraction of KCl and $(1 - x)$ mole fraction of KBr. When an equation is given for a physical property, p represents the property for the mixed crystal AB_xC_{1-x} and p_1 and p_2 are the values for the pure crystals AB and AC, respectively.

1. Introduction

A mixed crystal is obtained by crystallizing together two isomorphous crystals like KCl and KBr. Isomorphism is not the only condition for the formation of a mixed crystal; the lattice constants of the component crystals should be comparable. Tobolsky [1] showed that for ionic crystals like alkali halides complete miscibility is possible only above a temperature T given by $T = 4.5\delta^2$, δ being the percentage difference in lattice constants. For alkali halides at room temperature δ takes a value of 8%. Recently, Bharadwaj and Roy [2] have shown that the miscibility depends on the pressure as well.

The distribution of the mixing atoms may take place in two ways: substitutionally or interstitially. In substitutional mixed crystals, again, there are two types: ordered and disordered. Alkali halide mixed crystals are of the completely disordered substitutional type.

A mixed crystal has physical properties analogous to those of the pure crystals. The composition dependence varies from system to system and from property to property. In many cases, the property changes monotonically with composition in a linear or nearly linear manner. Once the trend in composition dependence is established, we have a means to have a tailor-made crystal with a desired value for a given physical property. In a few properties, the composition dependence is highly non-linear and, in some cases, the magnitude of the physical property for the mixed

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crystal even exceeds the values for the end members. In such a case, it is as if we have a new crystal in the family. Such behaviour is shown, for instance, in the microhardness of alkali halide mixed crystals. In some instances, mixed crystals show exciting behaviour. One such example is the appearance of a first-order Raman spectrum in mixed crystals of alkali halides which is absent in the pure crystals.

Interesting and important as the alkali halides are, no less important are their mixed crystals. Sixteen pairs of alkali halides are completely miscible at room temperature and several have limited miscibility. Some of these mixed crystals have found applications as information storage devices [3], as laser window materials [4, 5] and as neutron monochromators [6]. There is considerable work on the physical properties of alkali halide mixed crystals but it is scattered in the literature. Kitaigorodsky's treatise [7] on mixed crystals covers a very wide range of mixed crystals; as a consequence, the alkali halide mixed crystals have not been treated in any great detail. Hari Babu and Subba Rao [8] have recently reviewed aspects of the growth and characterization of alkali halide mixed crystals.

In the present review, several physical properties of alkali halide mixed crystals are considered. The trends in experimental data are analysed with particular reference to the composition dependence. Theoretical interpretations are discussed. We have not included a discussion of dislocations, ionic conductivity, microhardness and colour centres as these properties have been discussed at length in the review by Hari Babu and Subba Rao [8], although we refer to some of their conclusions. Our discussion is mainly confined to alkali halide mixed crystal systems with NaCl structure; there is not much work on systems with the CsCl structure.

2. Growth, characterization and composition determination of mixed crystals

Out of the seventeen alkali halides having NaCl structure, fifteen are soluble in water. It is possible to grow mixed crystals by evaporation of aqueous solution. However, the melt technique is commonly employed and single crystals with linear dimensions of several centimetres have been obtained.

Aspects of crystal growth and the characterization of alkali halide mixed crystals have been reviewed in detail by Hari Babu and Subba Rao [8]. Veeresham *et al.* [9] have grown single crystals of the mixed crystal systems KCl–KBr, KCl–KI, KBr–KI and KCl–NaCl. In all these systems, they found that the dislocation density increases with the degree of mixing and is maximum at the equimolar composition. Subba Rao and Hari Babu [10, 11] studied the microhardness of KCl–KBr and KBr–KI systems and found that the composition variation is similar to that of dislocation densities. Thus the mixed crystals, while retaining the properties of the pure crystals, have the advantage of a larger mechanical strength. Small-angle X-ray scattering studies [12] and diffuse X-ray scattering studies [13] of KCl–KBr mixed crystals have shown the absence of clusters or order. Freund *et al.* [6] grew KCl–KBr single crystals with a continuous variation of composition from one end to the other. Padiyan and Mohanlal [14] have grown a quaternary mixed crystal $K_{0.5}Rb_{0.5}Cl_{0.5}Br_{0.5}$.

If the mixed crystals are grown from solution, there can be a considerable difference between the composition of the starting mixture and that of the resulting crystal. This difference is much less when the melt technique is employed. However, significant differences in composition do exist from region to region of a crystal. Local variations in composition up to 20% were observed in KCl–KBr crystals [12]. In studies of the composition dependence of properties of mixed crystals, the accurate determination of composition is as important as the determination of the property itself.

For alkali halide mixed crystals with anionic substitution, the method of potentiometric titration [10] can be used for composition determination. In the case of cationic substitution, the techniques of atomic absorption spectroscopy [15] and X-ray fluorescence [16] are useful. Since the lattice constants can be determined accurately and the law of composition dependence of lattice constants is fairly well established, it affords a simple but reliable method for composition estimation which can be used for mixed crystals with anionic as well as cationic substitution [16, 17]. Nair and Walker [12] determined the composition of KCl–KBr mixed crystals from the measured macroscopic densities assuming an additivity rule. Recently, Rao *et al.* [18] proposed a method of composition estimation of mixed crystals from the Compton scattering of gamma rays. The method is non-destructive but time-consuming (seven days for a sample).

3. Composition dependence of physical properties

3.1. Lattice constants

The composition dependence of lattice constants in a mixed crystal series can be expressed by a general relation of the type

$$a^n = xa_1^n + (1 - x)a_2^n \qquad (1)$$

Different values have been proposed for the exponent n. When $n = 1$, Equation 1 becomes

$$a = xa_1 + (1 - x)a_2 \qquad (2)$$

This equation, which predicts a linear composition dependence, was suggested empirically by Vegard [19] and is known as Vegard's law.

If the volumes are assumed to be additive, we get

$$a^3 = xa_1^3 + (1 - x)a_2^3 \qquad (3)$$

This equation is known as Retger's rule and represents an ideal mixed crystal. Zen [20] pointed out that if the difference between a_1 and a_2 is very small, Equation 3 is indistinguishable from Equation 2.

Expressing the lattice energy U of an ionic crystal as

$$U = \frac{-Ae^2}{r} + \frac{b}{r^9} \qquad (4)$$

Grimm and Herzfeld [21] showed that the exponent n in Equation 1 is related to the power of r in the second

TABLE I Lattice constant *a* (nm) of some alkali halide mixed crystal systems

$KCl_xBr_{(1-x)}$ [10]		$K_xRb_{(1-x)}I$ [15]		$NaCl_xBr_{(1-x)}$[26]		$Na_xK_{(1-x)}Cl$ [27]		$K_xRb_{(1-x)}Cl$ [28]	
x	*a*	*x*	*a*	*x*	*a*	*x*	*a*	*x*	*a*
0	0.66008	0	0.7346	0	0.5956	0	0.62916	0	0.6592
0.15	0.65623	0.10	0.7314	0.215	0.5884	0.100	0.62354	0.338	0.6491
0.286	0.65064	0.22	0.7294	0.370	0.5840	0.300	0.61185	0.525	0.6431
0.460	0.64594	0.30	0.7269	0.495	0.5710	0.383	0.60654	0.913	0.6322
0.615	0.64096	0.40	0.7242	0.740	0.5658	0.500	0.59913	1.000	0.6292
0.864	0.63360	0.50	0.7222	1.000	0.5638	0.504	0.59883		
1.000	0.62741	0.62	0.7172			0.598	0.59256		
		0.75	0.7133			0.699	0.58571		
		0.87	0.7106			0.824	0.57705		
		1.00	0.7066			0.900	0.57156		
						1.000	0.56400		

term in Equation 4 and is equal to 8, giving

$$a^8 = xa_1^8 + (1 - x)a_2^8 \qquad (5)$$

Recent data for the lattice constants of the KCl–KBr, KCl–RbCl, KCl–NaCl, KBr–KI and NaCl–NaBr systems are given in Table I. Several investigators have tried to fit their data to one of the three equations given above (Equations 2, 3 and 5). Instead of comparing observed values of the lattice constant (a_E) with values calculated (a_C) from the equations, Slagle and McKinstry [22] compared values of ($a_E - a_C$) corresponding to these equations. This appears to be a more sensitive way of testing the above equations. The conclusions of various authors regarding the form of Equation 1 as tested on several systems are summarized in Table II. The bulk of the evidence indicates that the composition dependence of lattice constants in alkali halide mixed crystal systems is best represented by Vegard's law (Equation 2).

Mahapatra and Padhi [23] obtained the lattice constants for the KCl–KBr system by a novel method. From the Compton profile, the autocorrelation factor was determined which, in turn, yielded the lattice constant. The lattice constant, thus determined, was found to obey Vegard's law.

The KCl–NaCl system shows the largest deviation from Vegard's law [10], but it must be noted that this system has the poorest stability among the alkali halide mixed crystal systems. Evidence of some order has been obtained only in the KCl–NaCl system [24].

Kempter and Elliott [25] studied the lattice constants of UO_2–ThO_2 mixed crystals at high temperature and observed that the deviations from Equation 3 increase with increasing temperature. Such studies have not been made on the alkali halide mixed crystals.

3.2. Density and molar volume

It is surprising that measured values of the density, a simple but useful and fundamental quantity, are not available for all the mixed crystal systems of alkali halides. Barrett and Wallace [27] determined the densities of the KCl–NaCl system. Wollam and Wallace [31] carried out pycnometric measurement of the densities of the KCl–KBr and NaCl–NaBr systems. Slagle and McKinstry [32] measured the densities of KCl–KBr mixed crystals. The data obtained by these investigators are given in Table III.

Barrett and Wallace [27] and Wollam and Wallace [31] have calculated the densities of mixed crystals of KCl–NaCl, KCl–KBr and NaCl–NaBr from the lattice constants. These X-ray densities were found to be systematically higher than the pycnometric values for the mixed crystals; further, the difference was larger in the equimolar region. From this difference in densities, Barrett and Wallace [27] estimated the number of Schottky defects which was found to be large in the equimolar region.

From the values of the measured density, we have calculated the molar volume. The variation of molar volume with composition is shown in Fig. 1 for the KCl–KBr, NaCl–NaBr and KCl–NaCl mixed crystal systems. The composition dependence of the volume is linear in the KCl–KBr and NaCl–NaBr systems; very slight positive deviations from linearity are observed in the NaCl–KCl system.

3.3. Bulk modulus and compressibility

Values of the bulk modulus and its reciprocal, the compressibility, are not available from direct compression experiments but can be obtained from the elastic constants using the relation

$$K = \frac{1}{\psi} = \frac{C_{11} + 2C_{12}}{3} \qquad (6)$$

Values of the bulk modulus for the KCl–KBr [32], KCl–RbCl [33], KCl–NaCl [34] and KBr–KI [35] systems calculated from room-temperature data on

TABLE II Summary of studies on the composition dependence of lattice constants

System	Authors	Law of composition dependence (value of *n* in Equation 1)
KCl–KBr	Havighurst *et al.* [29]	1, 3
	Slagle and McKinstry [22]	3
	Subba Rao and Hari Babu [10]	1
	Mahapatra and Padhi [23]	1
KBr–KI	Nair and Walker [16]	3
KI–RbI	Van Den Bosch *et al.* [15]	1
	Fertel and Perry [30]	1
NaCl–NaBr	Avericheva *et al.* [26]	1
KCl–NaCl	Barrett and Wallace [27]	3
KCl–RbCl	Gnaedinger [28]	1

TABLE III Pycnometric and X-ray densities, d (10^3 kg m^{-3}), of mixed crystals

$KCl_{(1-x)}Br_x$			$NaCl_{(1-x)}Br_x$			$Na_xK_{(1-x)}Cl$		
x	d		x	d		x	d	
	Pycnometric	X-ray		Pycnometric	X-ray		Pycnometric	X-ray
Wollam and Wallace [31]			Wollam and Wallace [31]			Barrett and Wallace [27]		
0.00	1.987	1.986	0	2.1615	2.1630	0	1.9880	1.9881
0.20	2.156	2.160	0.1000	2.2829	2.2848	0.1002	1.9964	1.9982
0.30	2.238	2.239	0.1997	2.3971	2.3987	0.2997	2.0117	2.0217
Slagle and McKinstry [32]			0.2996	2.5069	2.5123	0.4999	2.0368	2.0538
0	1.984		0.3991	2.6169	2.6220	0.6990	2.0683	2.0922
0.168	2.129		0.4993	2.7203	2.7244	0.9003	2.1321	2.1363
0.171	2.126		0.5991	2.8255	2.8284	1.0000	2.1615	2.1630
0.382	2.302		0.7987	3.0160	3.0228			
0.387	2.300		1.0	3.1980	3.1992			
0.578	2.453							
0.598	2.473							
0.80	2.613							
1.0	2.744							

elastic constants are given in Table IV and are shown in Fig. 2.

The composition dependence of the bulk modulus is nearly linear in the KCl–KBr, KBr–KI and KCl–RbCl systems. A careful examination reveals a slight negative deviation from linearity. The maximum deviation is about 2% in the equimolar region in the KCl–KBr system. This deviation will be discussed later. In the KCl–NaCl system, the negative deviation from linearity is large (~ 15%) in the potassium-rich region. It may be noted that the KCl–NaCl system has a poor stability. Further, for this system, bulk modulus data are available only in the potassium-rich and sodium-rich regions and is lacking in the intermediate range of compositions. Hence, we shall not give much weightage to observations on this system and conclude that, in general, the composition dependence of the bulk modulus in alkali halide mixed crystals is nearly linear with a slight negative deviation from linearity.

Fancher and Barsch [36, 37] proposed the following functional form for ΔK (the difference between the experimental value of the bulk modulus and that expected from a linear composition dependence):

$$\Delta K = Dx(1 - x) \tag{7}$$

Assuming the additivity of volumes, Fancher and Barsch [36, 37] obtained the following expression for D:

$$D = \frac{[(K_1 V_2)^2 - (K_2 V_1)^2](K_2 - K_1)}{2K_1 K_2 V_1 V_2} \tag{8}$$

The values calculated from Equation 7 are shown in Fig. 3, along with those obtained from the experimental

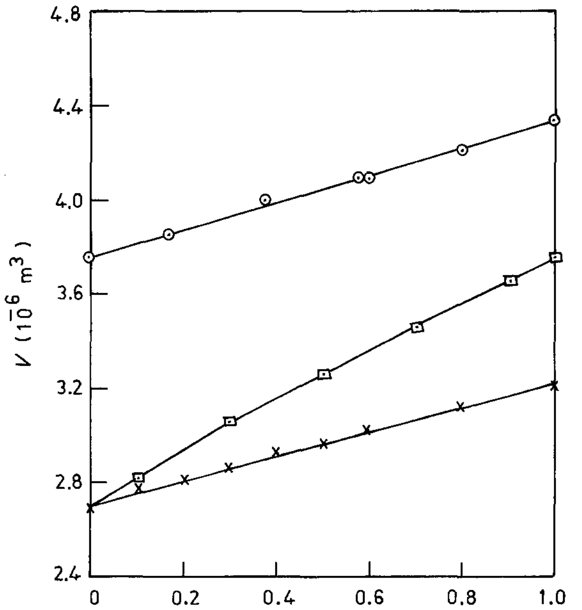

Figure 1 Composition dependence of molar volume: (⊙) $KCl_{(1-x)}Br_x$, (×) $NaCl_{(1-x)}Br_x$, ⊡ $Na_{(1-x)}K_xCl$.

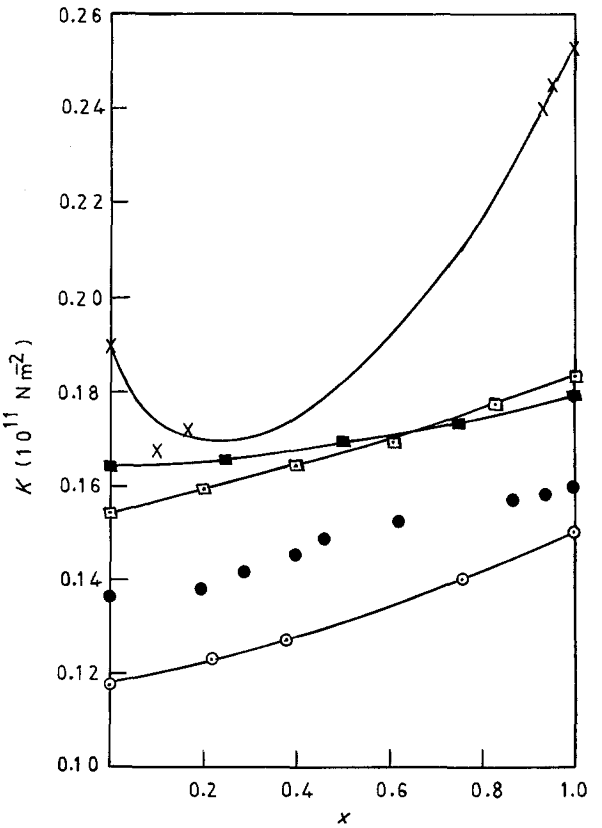

Figure 2 Composition dependence of bulk modulus: (●) $KCl_xBr_{(1-x)}$ [38]; (⊡) $KCl_xBr_{(1-x)}$ [32]; (■) $K_xRb_{(1-x)}Cl$ [33]; (×) $K_{(1-x)}Na_xCl$ [34]; (⊙) $KBr_xI_{(1-x)}$ [35].

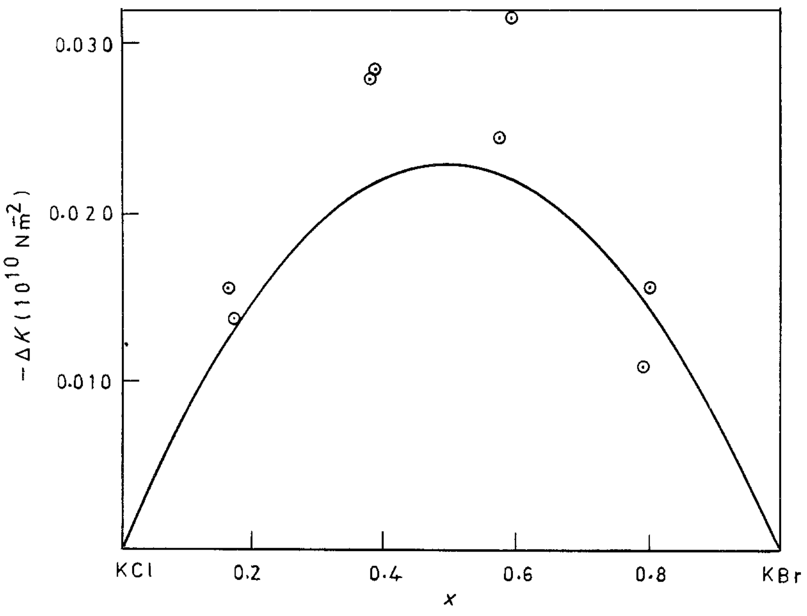

Figure 3 Composition dependence of ΔK for KCl–KBr system: (⊙) experimental values [32], (——) Equation 7.

data of Slagle and McKinstry [32]. Fancher and Barsch [36, 37] observed that the two sets of values (experimental and calculated from Equation 7) agree fairly well though not perfectly. The lack of perfect agreement was attributed partly to experimental error.

Shanker and Jain [38] made an attempt to calculate the bulk modulus of mixed crystals of alkali halides from a Born–Mayer type of potential energy function. They assumed a potential function, U, of the form

$$U = U_C + U_V + U_R \qquad (9)$$

Here U_C, U_V and U_R represent the contributions of the Coulomb, van der Waals and repulsive interactions, respectively. The repulsive interaction was considered up to the second neighbours. In the van der Waals terms, cross-interactions between the mixing ions (namely chlorine and bromine in KCl–KBr) were included. The various parameters in the potential function were estimated from those for the end members, and the bulk modulus was obtained from the relation

$$K = \frac{1}{18r}\frac{d^2U}{dr^2} \qquad (10)$$

Shanker and Jain [38] compared the values of K calculated in this way with experimental values and concluded that the agreement between theory and experiment was quite satisfactory. However, the "experimental" values quoted by Shanker and Jain are not truly experimental values; they are values obtained by linear interpolation of the bulk modulus values of the end members [5]. The values calculated by Shanker and Jain for the KCl–KBr system are shown in Fig. 2 along with the experimental values of Slagle and McKinstry [32]. It can be seen that the calculated values are systematically less than the experimental values by about 13% over the entire composition range (including the end members).

The composition dependence of the compressibility of the alkali halide mixed crystal is also nearly linear. The deviations from linearity are slight but positive. Varotsos and Alexopoulos [39] proposed a theoretical interpretation of the observed composition dependence of the compressibility of mixed crystals which takes into account the volume change in a crystal due to the creation of defects. This change in volume is given by

$$V = V^0 + n(v^d + v^0) \qquad (11)$$

Here, V and V^0 are respectively the molar volumes of the mixed crystal and the pure crystal, say KCl. v^0 is the volume of a molecule of KCl (in the KCl crystal) and v^d the defect volume. n is the number of defects, i.e. the number of KBr molecules introduced in the KCl lattice, and $(v^d + v^0)$ represents the change in volume when a KCl molecule is replaced by a KBr molecule. By differentiation of Equation 11, we get

$$\psi V = \psi^0 v^0 + n(\psi^d v^d + \psi^0 v^0) \qquad (12)$$

where ψ, ψ^0 and ψ^d represent the compressibilities of

TABLE IV Bulk modulus, K (10^{11} N m^{-2}), of some alkali halide mixed crystals

$KCl_xBr_{(1-x)}$ [32]		$K_xRb_{(1-x)}Cl$ [33]		$K_xNa_{(1-x)}Cl$ [34]		$KBr_xI_{(1-x)}$ [35]	
x	K	x	K	x	K	x	K
0	0.154	0	0.163	0	0.253	0	0.118
0.200	0.159	0.25	0.165	0.038	0.244	0.220	0.123
0.402	0.164	0.50	0.169	0.058	0.240	0.385	0.126
0.422	0.164	0.75	0.173	0.824	0.172	0.765	0.140
0.613	0.169	1.00	0.179	0.900	0.168	1.0	0.150
0.618	0.169			1.0	0.190		
0.829	0.176						
0.832	0.177						
1.0	0.183						

TABLE V The compressibilities of mixed crystals in the $KCl_xBr_{(1-x)}$ system

x	$\psi(10^{-11}\,N^{-1}\,m^2)$	
	Calculated from Equation 15	Experimental [32]
0	–	6.482
0.200	6.236	6.309
0.205	6.241	6.284
0.402	6.071	6.135
0.422	6.041	6.099
0.613	5.844	5.903
0.618	5.854	5.905
0.829	5.662	5.656
0.832	5.643	5.659
1.0	–	5.464

TABLE VI Room-temperature values of the second-order elastic constants of mixed crystals $KCl_xBr_{(1-x)}$, C_{ij} $(10^{10}\,N\,m^{-2})$

Slagle and McKinstry [32]				Sharko and Botaki [41]			
x	C_{11}	C_{12}	C_{44}	x	C_{11}	C_{12}	C_{44}
0	3.468	0.580	0.507	0	3.468	0.522	0.507
0.200	3.545	0.605	0.531	0.245	3.546	0.546	0.528
0.205	3.544	0.615	0.530	0.395	3.630	0.606	0.544
0.402	3.630	0.630	0.552	0.51	3.665	0.625	0.558
0.422	3.665	0.632	0.557	0.74	3.782	0.674	0.585
0.613	3.762	0.660	0.580	1.0	3.989	0.725	0.625
0.618	2.764	0.658	0.581				
0.829	3.922	0.691	0.608				
0.832	3.925	0.688	0.607				
1.00	4.069	0.711	0.631				

the mixed crystal, the host crystal and of the defect volume, respectively. Varotsos and Alexopoulos [39] use a result obtained by them earlier [40] according to which

$$\psi^d = \psi^0 - \frac{d^2K_0}{dP^2}\left[\frac{dK_0}{dP} - 1\right]^{-1} \tag{13}$$

where K_0 is the bulk modulus of the host crystal and P the pressure. At this stage, Varotsos and Alexopoulos [39] make use of the Born potential for an ionic crystal

$$U = -\frac{Ae^2}{r} + \frac{b}{r^m} \tag{14}$$

where the symbols have the usual significance. From Equation 14, the first and second pressure derivatives of K_0 are obtained and substituted in Equation 13. Finally, the substitution of Equation 13 in Equation 12 gives

$$\psi = \psi^0\frac{V^0}{V}\left(1 + \frac{n}{N}\right) + \psi^0\frac{n}{N}\frac{Nv^d}{V}\frac{1 + 4(m + 3)}{3(m + 4)} \tag{15}$$

v^d is obtained from the measured densities by the use of Equation 11. The estimation of the compressibility ψ of the mixed crystal from Equation 15 requires a knowledge of the compressibility ψ^0 of the host crystal and the measured density of the mixed crystal. The values of the compressibility obtained by Varotsos and Alexopoulos [39] for the KCl–KBr system are given in Table V along with experimental values from the data of Slagle and McKinstry [32]. The calculated values agree with the experimental values within 0.3 to 0.6%, which is within the experimental error.

3.4. Second-order elastic constants (SOEC), third-order elastic constants (TOEC) and pressure derivatives of SOEC

The SOEC for alkali halide mixed crystals are available for the following systems: KCl–KBr [32, 41], KBr–KI [35], KCl–RbCl [33], KCl–NaCl [34] and NaCl–NaBr [42].

Slagle and McKinstry [32] measured the SOEC for several compositions in the KCl–KBr system at room temperature and for four compositions at elevated temperatures up to 400° C. Sharko and Botaki [41] made measurements from low temperatures up to room temperature. The room-temperature values of the SOEC for the KCl–KBr system from both the sources are given in Table VI.

The values given by Slagle and McKinstry [32] are shown in Fig. 4 to indicate the composition dependence. Regarding the composition dependence of the

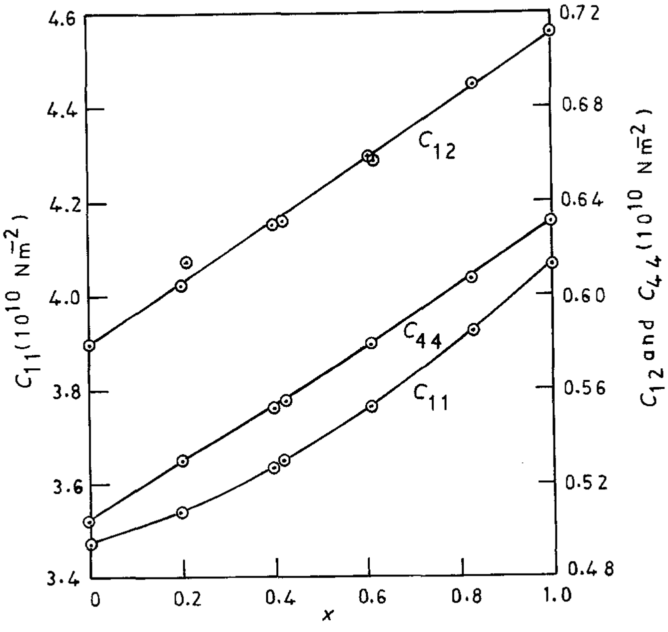

Figure 4 Composition dependence of second-order elastic constants for the $KCl_xBr_{(1-x)}$ system.

elastic constants of KCl–KBr crystals, Slagle and McKinstry [32] comment that when the elastic constants C_{11} and C_{44} are plotted against composition, the resultant curve is not a straight line but a curve concave upward and that the experimental uncertainty in C_{12} does not allow a better description than linear dependence. Fancher and Barsch [36, 37] examined Slagle and McKinstry's data and concluded that C_{12} and C_{44} vary linearly with composition but C_{11} "hangs" up to two per cent below the straight line joining the values for the end members. Sebastian [43] observed that the SOEC of $KCl_xBr_{(1-x)}$ crystals can be represented by the equations

$$C_{11} = x(C_{11})^{-3}_{KCl} + (1 - x)(C_{11})^{-3}_{KBr} \quad (16)$$

$$C_{12} = x(C_{12})_{KCl} + (1 - x)(C_{12})_{KBr} \quad (17)$$

$$C_{44} = x(C_{44})_{KCl} + (1 - x)(C_{44})_{KBr} \quad (18)$$

Recently, Basu *et al.* [44] theoretically investigated the composition dependence of the SOEC of alkali halide mixed crystals. Combining the pseudo-unit cell model of Chang and Mitra [45] for the mixed crystal and the deformable shell model of Basu and Sengupta [46] for the lattice dynamics, they obtained expressions for the three static elastic constants of the mixed crystal $AB_xC_{(1-x)}$. These expressions involve six parameters pertaining to each of the end members. The values of the static elastic constants for various compositions in the KCl–KBr system calculated by Basu *et al.* [44] from their theory agree with the experimental values of Slagle and McKinstry [32] within 1%.

The composition dependence of SOEC does not seem to be the same in all mixed crystal systems of alkali halides. Thus, in the KBr–KI system [35] all the elastic constants show a non-linear composition dependence with negative deviations from linearity. The maximum deviation is about 3% in all the elastic constants in the equimolar region. In the KCl–RbCl system [33], the elastic constant C_{44} shows non-linear composition dependence in addition to C_{11}. In the KCl–NaCl system [34] the trend is different.

Apart from the study of one mixed crystal, namely $KCl_{0.923}Br_{0.077}$ [47], there is no experimental work on the TOEC and the pressure variation of SOEC of mixed crystals.

Varotsos and Alexopoulos [39] obtained an expression for the pressure derivative of bulk modulus of mixed crystals on the basis of the model discussed earlier and made estimates of d*K*/d*P* for various compositions in the $KCl_xBr_{(1-x)}$ system. Shanker and Jain [38] also calculated d*K*/d*P* for the KCl–KBr system from an interatomic potential. The values of d*K*/d*P* obtained by Varotsos and Alexopoulos [39] and Shanker and Jain [38] are plotted in Fig. 5, along with the experimental values for KCl, KBr and $KCl_{0.923}Br_{0.077}$. It is seen that the values of Shanker and Jain are systematically lower than those of Varotsos and Alexopoulos by about 20%. Further, the experimental values for KCl, KBr and the single mixed crystal are close to the values of Varotsos and Alexopoulos. This indicates that the concept of defect volume compressibility introduced by Varotsos and Alexopoulos [39] plays an important role in determining the elastic behaviour of mixed crystals. However, to confirm this point, further experimental data for various compositions in the KCl–KBr system and also other mixed crystal systems are desirable.

Singh *et al.* [48] have made theoretical estimates of the TOEC and pressure derivatives of SOEC for the NaCl–NaBr system, but experimental values are not available for comparison.

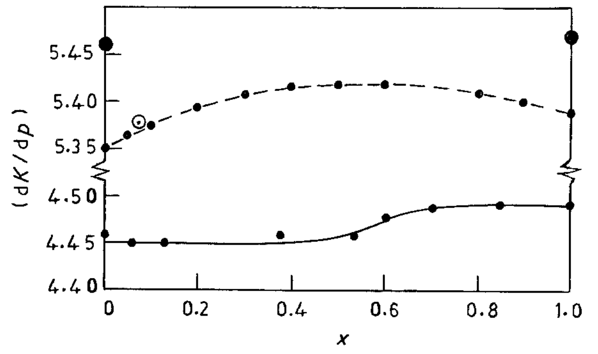

Figure 5 Composition dependence of pressure derivative of bulk modulus for the $KCl_{(1-x)}Br_x$ system: (– – –) [39], (——) [38], (⊙) [47], (●) [38].

3.5. Static dielectric constant

There is very little work on the dielectric constant of mixed crystals. Fertel and Perry [30] were the first to determine the static dielectric constant of the KCl–KBr system. The values were obtained by Kramers–Kronig analysis of infrared reflectivity curves of the crystals. Subsequently Kamiyoshi and Nigara [49] studied this system. They made measurements at 1 MHz by the immersion method. The values obtained in these two experiments are given in Table VII and are also shown in Fig. 6. This is the only system for which results on dielectric constant are

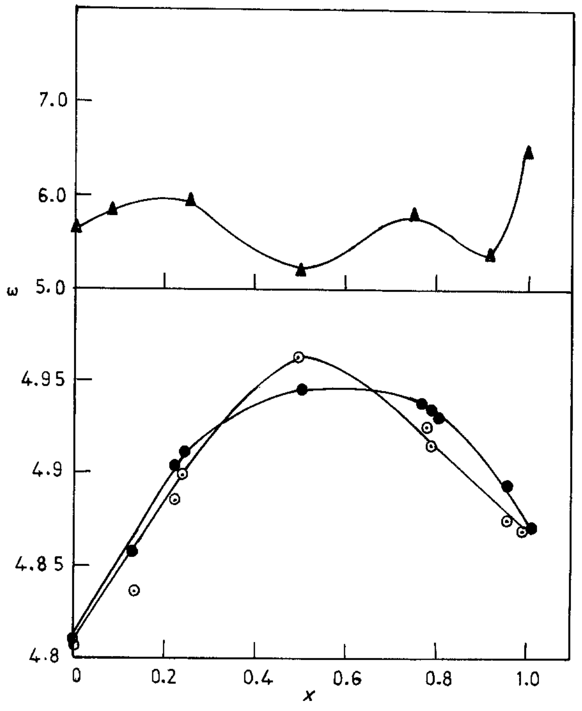

Figure 6 Composition dependence of static dielectric constant for the $KCl_{(1-x)}Br_x$ system: (▲) [30], (⊙) [49], (●) [50].

TABLE VII Values of static dielectric constants for the $KCl_{(1-x)}Br_x$ system

x	ε	x	ε	
	[30]		[49]	[50]
0	5.4	0	4.81	4.812
0.08	5.8	0.15	4.84	4.865
0.25	5.9	0.22	4.89	4.911
0.50	5.1	0.23	4.90	4.912
0.75	5.8	0.53	4.96	4.948
0.92	5.4	0.77	4.93	4.943
1.0	6.5	0.78	4.93	4.938
		0.80	4.91	4.935
		0.96	4.88	4.891
		1.0	4.87	4.871

available from infrared reflectivity and also from direct measurement. However, as can be seen from Fig. 6 there is a serious discrepancy between the two sets of values. Recently, a systematic study of the KCl–KBr system has been carried out by Sirdeshmukh and Prameela Devi [50]. Their results are also included in Table VII. It is seen that these new results confirm the results obtained by the Japanese workers.

Kamiyoshi and Nigara [49] also made measurements on four other systems, namely NaCl–NaBr, RbCl–RbBr, KCl–RbCl and KBr–KI. In all these systems it was found that the composition dependence of dielectric constant is slightly non-linear, with positive deviation from linearity.

Kamiyoshi and Nigara [49] proposed the following equation for the dielectric constant of a mixed crystal in terms of its composition:

$$\begin{aligned}\frac{\varepsilon - 1}{\varepsilon + 2} = {} & x\left(\frac{\lambda}{\lambda_1}\right)^2\left(\frac{a_1}{a}\right)^6\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \\ & + (1 - x)\left(\frac{\lambda}{\lambda_2}\right)^2\left(\frac{a_2}{a}\right)^6\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} \\ & + x\left(\frac{a_1}{a}\right)^3\left[1 - \left(\frac{\lambda}{\lambda_1}\right)^2\left(\frac{a_1}{a}\right)^3\right]\frac{R_1^2 - 1}{R_1^2 + 2} \\ & + (1 - x)\left(\frac{a_2}{a}\right)^3\left[1 - \left(\frac{\lambda}{\lambda_2}\right)^2\left(\frac{a_2}{a}\right)^3\right]\frac{R_2^2 - 1}{R_2^2 + 2} \end{aligned} \tag{19}$$

This equation was obtained by a combination of the Clausius–Mosotti equation and the Lorentz–Lorenz equation and was based on the assumption that the ionic polarizabilities for mixed crystals are strongly dependent on the lattice constant. The lattice constant and polarizabilities vary according to the empirical relations

$$a = a_1 + (1 - x)(a_2 - a_1) \tag{20}$$

$$\lambda = \lambda_1 + (1 - x)(\lambda_2 - \lambda_1) \tag{21}$$

This interpolation equation requires the knowledge of lattice constants, the refractive index, the dielectric constant and infrared absorption wavelength (λ) for the pure crystals. Recently Varotsos [51] re-examined this equation and tried to provide a theoretical justification. He started with the Clausius–Mosotti equation and expressed the polarizabilities in terms of an electronic component and an ionic component. By adopting suitable expressions for the polarizability Varotsos [51] obtained the equation

TABLE VIII Experimental and calculated refractive indices of $KCl_xBr_{(1-x)}$ mixed crystal system

x	R	
	Experimental	Calculated
0	1.5593	
0.2	1.5433	1.5474
0.4	1.5330	1.5345
0.6	1.5209	1.5208
0.8	1.5047	1.5060
1.0	1.4902	

$$\begin{aligned}\frac{\varepsilon - 1}{\varepsilon - 2} = {} & \frac{1}{a^3}\left[x\left(\frac{a_1^3(R_1^2 - 1)}{R_1^2 + 2} - \frac{a_2^3(R_2^2 - 1)}{R_2^2 + 2}\right)\right. \\ & \left. + \frac{a_2^3(R_2^2 - 1)}{R_2^2 + 2}\right] \\ & + \frac{4}{3\varepsilon_0 a^4}\left(\frac{1}{m_A} + \frac{x}{m_B} + \frac{1 - x}{m_c}\right)^{-1} \\ & \times \left(\frac{x\beta a_1 K_1}{\mu_1 K} + \frac{\gamma(1 - x)a_2 K_2}{\mu_2 K}\right) \end{aligned} \tag{22}$$

Here ε_0 is the vacuum dielectric constant. β and γ are the values of the ionic polarizabilities for KCl and KBr, respectively. m_A, m_B and m_C are respectively the masses of atoms A, B and C in a mixed crystal of type AB_xC_{1-x}. This equation needs only three quantities, namely lattice constants, refractive index and the bulk modulus of the end members. Data on bulk modulus for mixed crystals are available for several systems. Alternatively the bulk modulus of the mixed crystals can be calculated from the values of the pure crystals by the method of Varotsos and Alexopoulos [39]. Varotsos [51] found that the results obtained from this equation agree well with the experimental results. Thus the equation gives a value of 4.937 for the dielectric constant of $KCl_{0.4}Br_{0.6}$ which agrees well with experimental value 4.94.

3.6. Optical and piezo-optic properties

Refractive index measurements have been made only on the KCl–KBr system. Using an Abbe refractometer and Na–D light, Nigara and Kamiyoshi [52] determined the refractive index. They observed that the experimental values of the refractive index agreed well with those calculated from the Lorentz–Lorenz formula (Table VIII).

The alkali halides are optically isotropic but develop birefringence when subjected to uniaxial stress. Measurements of the piezo-optic birefringence of pure alkali halides have been made by Bansigir and Iyengar [53]. Bansigir and Iyengar [54] proposed a theory for the piezo-optic birefringence of alkali halides by taking into account the effects of change in density as well as change in polarizability on the refractive index. An experimental study of the piezo-optic birefringence in KCl–KBr mixed crystals has been made by Ethiraj *et al.* [55], who observed that the piezo-optic Brewster constants vary non-linearly with composition. Kumar *et al.* [56] showed that the

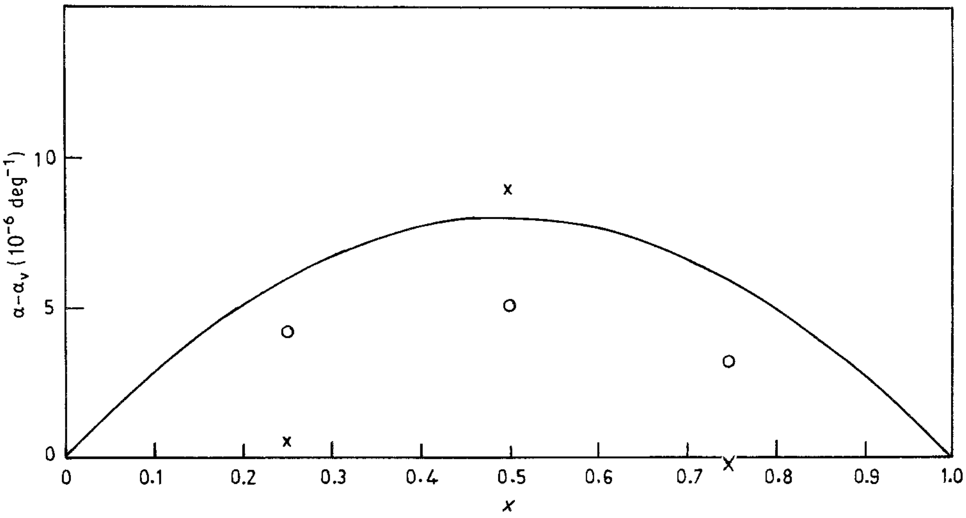

Figure 7 Composition dependence of the deviation of volume expansion from linearity ($\Delta\alpha$) for the KCl–KBr systems: (○) [58], (×) [57], (——) Equations 23.

observed variation can be accounted for by the theory of Bansigir and Iyengar [54].

3.7. Thermal expansion

Although there is considerable work on the thermal expansion of pure alkali halides, the work on mixed crystals is surprisingly scanty.

Kantola [57] made measurements on three compositions in the KCl–KBr system. Slagle and McKinstry [32] refer to their own measurements on the KCl–KBr system. The values are not given in the paper by Slagle and McKinstry but they comment that deviations from linearity are of the order of 2%. Salimaki [58] also made measurements on three compositions and found positive deviations from linearity.

Hietala [59, 60] developed a theory of heat of formation for solid solutions, and as a byproduct obtained the relation

$$\Delta\alpha = \frac{3}{T_v}\frac{\Delta r}{r}\frac{1-s}{1+s}x(1-x) \qquad (23)$$

where $\Delta\alpha$ is the deviation of the volume coefficient of expansion from linearity, T_v is the temperature at which Vegard's law is valid, Δr is the difference in lattice spacing of end members, r the lattice spacing of the mixed crystal and $s = r_2\psi_1/r_1\psi_2$. Although Equation 23 is very approximate and its validity is doubtful, the experimental results of Kantola [57] and Salimaki [58] plotted in Fig. 7 show qualitative agreement.

Ivankina and Pozdeeva [61] made measurements on the KCl–RbCl system at elevated temperatures. They observed that the values of the coefficient of thermal expansion deviate from linearity with maximum deviation at the equimolal composition; this deviation was found to decrease with increasing temperature and to vanish at 750° C.

3.8. Debye temperature

The Debye temperature is derivable from experimental data like specific heats, elastic constants, X-ray and neutron diffraction intensities, etc. Various methods of determination of Debye temperatures have been discussed in reviews by Blackman [62], Herbstein [63], Mitra [64] and Alers [65].

Several relations have been proposed either semi-theoretically or empirically to describe the composition dependence of the Debye temperatures of mixed crystals. Thus, by assuming the additivity of specific heats and using for the specific heat the low-temperature expression from Debye's theory (the Debye T^3 expression), the following relation is obtained:

$$\Theta^{-3} = x\Theta_1^{-3} + (1-x)\Theta_2^{-3} \qquad (24)$$

where Θ_1 and Θ_2 are the Debye temperatures of the end members and Θ that of the mixed crystal. This relation is known in literature as the Kopp–Neumann relation (See Swalin [66], for a discussion). Following the same procedure but employing the high-temperature expression for specific heats (Ghatak and Kothari [67]), Nagiah and Sirdeshmukh [68] obtained

$$\Theta^2 = x\Theta_1^2 + (1-x)\Theta_2^2 \qquad (25)$$

Karlsson [69] and Nagiah and Sirdeshmukh [68], respectively, proposed the following relations from empirical considerations:

$$\Theta^{-2} = x\Theta_1^{-2} + (1-x)\Theta_2^{-2} \qquad (26)$$

$$\Theta^{-1} = x\Theta_1^{-1} + (1-x)\Theta_2^{-1} \qquad (27)$$

A number of reports on the Debye temperature are available for several mixed crystal series of alkali halides. A summary of the reports is given in Table IX. From this summary it may be concluded that, in general, the composition dependence of the Debye temperatures of mixed crystals is slightly non-linear with negative deviations from linearity. By and large, the composition dependence is well described by the Kopp–Neumann relation (Equation 24).

3.9. The Debye–Waller factors and static distortion

The reduction of intensity of a diffracted X-ray or neutron beam due to the thermal vibrations in the

TABLE IX Summary of reports on the Debye temperatures of mixed crystals

System	Reference	Method	Conclusion regarding composition dependence
KCl–KBr	[69]	Specific heats	Equation 26 found suitable
	[41]	Elastic constants	Negative non-additivity observed
	[68]	Elastic constants	Equations 24, 25 and 27 tested and Equation 27 found most suitable
KCl–RbCl	[33]	Elastic constants	Deviation from linearity negligible
KCl–NaCl	[34]	Elastic constants	Deviation from linearity largest among alkali halide mixed crystal systems and attributed to low stability
KBr–KI	[35]	Elastic constants	Negative non-additivity
	[70]	Specific heats	Single composition ($KBr_{0.53}I_{0.47}$) studied; Equation 26 found suitable
KBr–RbBr	[17]	X-ray diffraction	Equation 24 found suitable
KI–RbI	[71]	Neutron diffraction	Equation 24 found suitable except for one composition ($K_{0.5}Rb_{0.5}I$)
KF–RbF	[72]	Neutron diffraction	Equation 24 found suitable
NaCl–NaBr	[26]	Elastic constants	Equation 24 found suitable

diffracting crystal is given by

$$I = I_0 \exp(-2B \sin^2\theta/\lambda^2) \qquad (28)$$

where I is the observed intensity, I_0 the intensity for the static crystal and θ the Bragg angle. B is known as the Debye–Waller factor. It has been shown theoretically that B is related to the mean square amplitude of atomic vibration and also to the Debye temperature [73].

The Debye–Waller factors of $KCl_{0.5}Br_{0.5}$ were determined by Wasastjerna [74] and Ahtee *et al.* [75] from X-ray intensities. Recently, Mohanlal *et al.* [76] determined the Debye–Waller factors for two compositions in the KCl–KBr system from neutron diffraction intensities. All these studies indicate that the Debye–Waller factors of mixed crystals are larger than those expected from additivity. In fact, the Debye–Waller factors in the equimolar region are considerably larger than those for either end member.

In a disordered mixed crystal, in which two kinds of atoms or ions are arranged on a set of atomic sites, small local distortions in the lattice arise because of the atoms of different sizes. The enhanced Debye–Waller factor is a consequence of this "size effect". Hietala [60], Borie [77], Weiss [78] and Dernier *et al.* [79] have proposed models to estimate the contribution of the local disorder (B') to the Debye–Waller factor. The Weiss model leads to the following expression for B'.

$$B' = 24x(1 - x)(a_1 - a_2)^2 \qquad (29)$$

The values of B' obtained from experiment and from Equation 29 for the KCl–KBr system are given in Table X. The agreement between experiment and theory is fair.

TABLE X Static distortion factors (B') for $KCl_xBr_{(1-x)}$ mixed crystals

x	$B'(10^{-2}nm^2)$	
	Experimental	Calculated*
0.2	0.34 ± 0.10†	0.362
0.4	0.47 ± 0.10†	0.543
0.5	0.513‡	0.566

*From Equation 29.
†Mohanlal *et al.* [76].
‡Wasastjerna [74].

Wasastjerna [74] also determined the Debye–Waller factors for $K_{0.5}Rb_{0.5}Cl$. Rcently, Srinivas and Sirdeshmukh [17] obtained the Debye–Waller factors for several compositions in the KBr–RbBr system from X-ray intensities. Their results (Fig. 8) also show that the composition dependence is highly non-linear, with values for intermediate compositions exceeding those of end members. Since a common Debye–Waller factor was assumed, a detailed comparison with the Weiss model is not possible.

3.10. Energetics of mixed crystals (cohesive energy and heat of formation)

The alkali halides are well described by the Born model for ionic crystals. The lattice energy can be expressed in one of the following forms:

$$U = -\frac{Ae^2}{r} + \frac{b}{r^n} \qquad (30)$$

$$U = -\frac{Ae^2}{r} + b\mathrm{e}^{-r/\varrho} \qquad (31)$$

In the above equations, the first term represents the Coulomb energy and the second term the repulsion energy due to overlap. b, n and ϱ are repulsion parameters which can be determined from the compressibility.

For mixed crystals of alkali halides, Tobolsky [1] used Equation 30. Wallace [80] employed Equation 31 but also included the van der Waal terms. Shanker

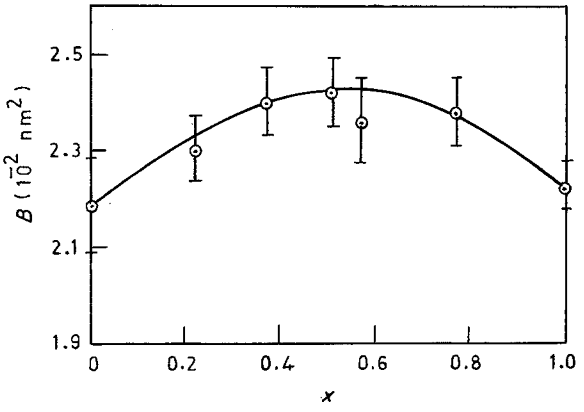

Figure 8 Composition dependence of Debye–Waller factor for the $K_xRb_{(1-x)}Br$ system.

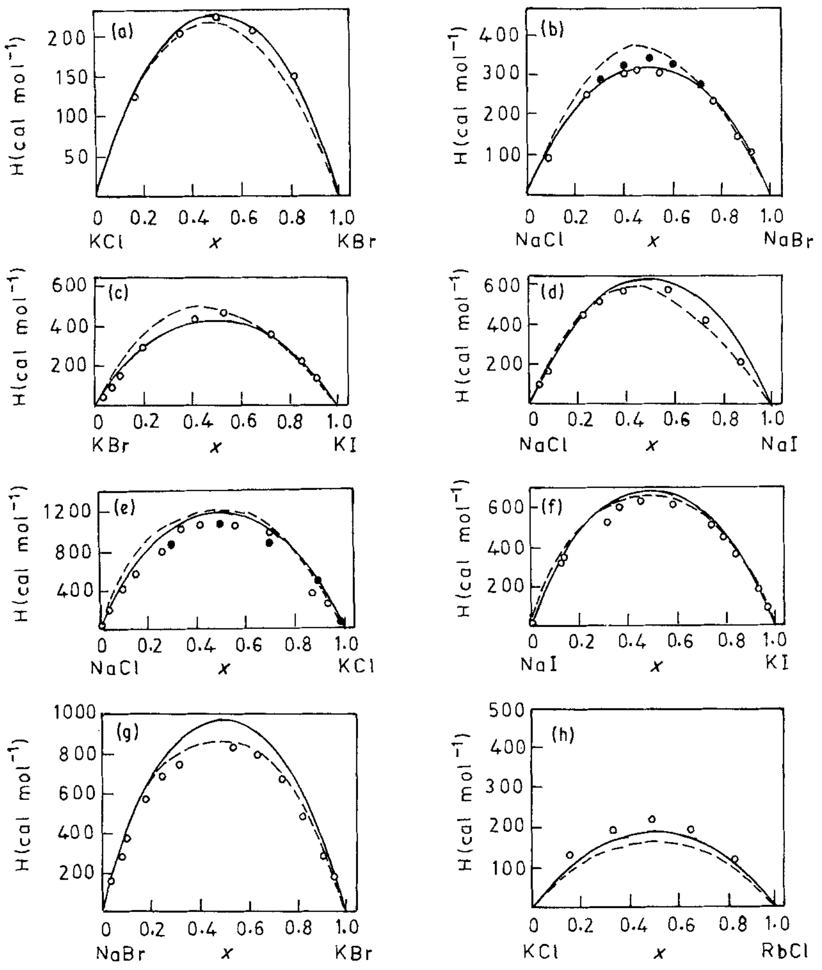

Figure 9 Composition dependence of heats of formation. Open and closed circles are experimental points: (a) KCl–KBr [81]; (b) NaCl–NaBr, (○) [84], (●) [83]; (c) KBr–KI (○) [84]; (d) NaBr–NaI [84]; (e) NaCl–KCl, (○) [84], (●) [27]; (f) NaI–KI [84]; (g) NaBr–KBr [84]; (h) KCl–RbCl [82]. Solid and dashed curves refer to theoretical values: (——) [89], (– – –) [36, 37].

and Jain [38] calculated the lattice energies of alkali halide mixed crystals using recent input data. "Experimental" values of the lattice energy are not available.

The formation of alkali halide mixed crystals is endothermic. The heat of formation is of the order of 0.2 to 0.6 kcal mol^{-1} (0.8 to 2.5 kJ mol^{-1}; compare this with the cohesive energy ~ 150 kcal mol^{-1} or 628 kJ mol^{-1}). Heats of formation for several alkali halide mixed crystals have been carefully measured [27, 81–84]. In all cases, the curve connecting the heat of formation and the composition is a vertical inverted parabola. Fineman and Wallace [83] showed that the experimental values of the heat of formation can be fitted to an empirical equation:

$$H = ax + bx^2 + cx^3 \qquad (32)$$

where a, b and c are constants.

Theoretically, the definition of the heat of formation is

$$H = U - [xU_1 + (1 - x)U_2] \qquad (33)$$

Several attempts have been made to theoretically account for the heats of formation. Tobolsky [1] and Wallace [80] calculated the heat of formation by substituting in Equation 33 the lattice energy values calculated by them, but they observed a large difference from the experimental values. Durham and Hawkins [85] pointed out that agreement with experimental values of heat of formation is possible only by considering an additional mechanism. Thus, they considered special configurations for the solute ions and calculated a "displacement energy" to be included in Equation 33. This improved the agreement somewhat. Fancher and Barsch [36, 37] used the model of Dick and Das [86, 87] for the relaxation of ions in the mixed crystals and obtained the "site energy". Twenty-six sites were allowed in the model. The calculation of the heat of formation for this model is lengthy but requires only limited input data (lattice constant, repulsive parameters and electronic polarizations). Fancher and Barsch's calculations gave reasonable agreement with experimental data in seven systems; only in the case of the KCl–RbCl system was the deviation significant.

Recently, Paul and Sengupta [88, 89] developed a simpler model in which the mixed crystal is treated as a defect crystal. The defect concentration is developed stepwise and in every step the defect crystal is considered as an equivalent perfect crystal with a modified lattice parameter. The agreement between calculated and experimental values of H is better in the systems with negative-ion substitution than in systems with positive-ion substitution.

The experimental values of H for eight systems are shown in Fig. 9 as a function of the composition along with values obtained theoretically by Fancher and Barsch [36, 37] and Paul and Sengupta [89].

3.11. Spectroscopic properties

Kruger *et al.* [90] were the first to record the IR spectra of alkali halide mixed crystals. They studied the NaCl–KCl system. Mitsuishi [91] recorded the IR spectra for mixed crystals in the KCl–KBr and KCl–RbCl systems. The KCl–KBr system was also studied by Ferraro *et al.* [92]. Recently Angress *et al.* [93] have recorded IR spectra for the KCl–RbCl and KBr–RbBr systems. In all these studies it has been observed that the frequency of the transverse optical mode varies linearly with composition. Fertel and Perry [30] obtained the IR frequency from the reflectivity data for the KCl–KBr system and reported a slightly non-linear dependence on composition.

An interesting observation was made by Fertel and Perry [30] in their study of the KI–RbI system. For this system they observed not just a single frequency as in the case of pure crystals but two frequencies close to those of the pure crystals. Angress *et al.* [93] observed two frequencies in the KCl–RbBr system. This is a new phenomenon and is referred to as "two-mode behaviour."

A phenomenological theory for the long-wavelength optic phonons of mixed crystals has been proposed by Chang and Mitra [45]. A criterion has been obtained to predict whether a given mixed crystal of type AB_xC_{1-x} will exhibit a one-mode or two-mode behaviour. The criterion is

$$m_B > \mu_{AC} \quad \text{one-mode behaviour}$$

$$m_B < \mu_{AC} \quad \text{two-mode behaviour}$$

where m_B is the mass of Atom B and μ_{AC} is the reduced mass of AC.

Pure alkali halides show only second-order Raman spectra [12, 16, 94]. But in the mixed crystals, the addition of one of the alkali halides to another alkali halide disturbs the symmetry of the pure crystal and a first-order Raman spectrum is observed in the mixed crystals. Thus, the appearance of a first-order Raman spectrum is a new phenomenon displayed by mixed crystals but not displayed by the pure members.

Nair and Walker [12] first studied the Raman spectrum of mixed crystals of the KCl–KBr system. Subsequently, they studied the KBr–KI, KCl–KI and KCl–RbCl systems [16]. The KCl–KBr, KBr–KI and KCl–KI systems involved negative-ion substitution. For these systems Nair and Walker found that the T_{2g} phonon did not show much variation but the A_{1g} phonon was found to vary linearly with composition. But the KCl–RbCl system involves positive-ion substitution. Here, the Raman spectra contain E_g and T_{2g} phonons. In this system, the E_g phonon was found to vary linearly with composition but not the T_{2g} phonon. The features in the observed first-order Raman spectra of alkali halide mixed crystals have been satisfactorily explained on the basis of a lattice dynamical model by Massa *et al.* [95, 96].

4. Discussion

Several physical properties of alkali halide mixed crystals have been discussed in the preceding section. Theoretical work on the lattice dynamics of mixed crystals is not included in the above discussion. Results on experimental phonon dispersion relations are also not included as they are too sparse at the moment. On the basis of the composition dependence, the physical properties of these mixed crystals can be grouped in four categories as follows:

TABLE XI Categorization of some physical properties of mixed crystals on the basis of their composition dependence (Type A, linear; Type B, slightly non-linear; Type C, highly non-linear; Type D, new phenomenon)

Property	Type			
	A	B	C	D
Lattice constant	xxxxxxxxxxxxxxxx			
Thermal expansion	xxxxxxx			
Bulk modulus		xxxxxxx		
Elastic constants	xxxxxxx			
Debye temperature	xxxxxxxxxxxxxxxx			
Refractive index	xxxxxxx			
Dielectric constant		xxxxxxxxxxxxxxxx		
Debye–Waller factor			xxxxxxx	
Dislocation density			xxxxxxx	
Microhardness			xxxxxxx	
Heat of formation			xxxxxxx	
IR spectra				
Single mode	xxxxxxxxxxxxxxxx			
Two modes				xxxxxxx
Raman spectra (1st order)				xxxxxxx

Type A: properties which show a linear composition dependence.

Type B: properties which show a slightly non-linear composition dependence.

Type C: properties which show a highly non-linear composition dependence with values for mixed crystals exceeding those for end members.

Type D: new phenomena (properties displayed by mixed crystals but not displayed by the pure crystals).

In Table XI, this grouping of the properties is shown. Some properties not discussed in this review but discussed elsewhere [8] are also included in the table.

Most of the properties show either a linear composition dependence (Type A) or a slightly non-linear composition dependence (Type B). This trend in the composition dependence is consistent with the facts that (i) these properties are, by and large, determined by the interatomic forces, (ii) the nature of the interatomic forces is the same for mixed crystals in a given series, and (iii) the magnitude of the interatomic interactions varies smoothly from one end member to the other.

The properties which show a highly non-linear composition dependence (Typce C) are influenced by additional factors not present in the pure crystals. Thus, the presence of a second atom at lattice points normally occupied by one atom results in a static displacement which enhances the Debye–Waller factor. This displacement (or strain) is also responsible for a higher dislocation density which in turn increases the microhardness. Although, on an average, the alkali halide mixed crystals are thoroughly disordered, the ions around a solute ion assume configurations of minimum energy. The observed heats of formation can be satisfactorily accounted for only by taking into consideration these site energies.

The substitution of a second ion (say bromine) in a host crystal (say KCl) affects the symmetry, at least locally. This gives rise to new features (Type D) in symmetry-dependent properties like the IR and

Raman spectra of mixed crystals. The removal of the centre of symmetry in some unit cells should also lead to optical rotation, a property not possessed by the pure alkali halides [56]. There is no clear experimental evidence in this regard although Slagle and McKinstry [32] refer to the observation of some optical rotation.

This review shows that not all the physical properties of mixed crystals have been thoroughly investigated. The properties of lattice constant, elastic constants, microhardness, dislocation densities, ionic conductivity and heats of formation have been investigated for several systems by several workers and the trends in the properties are clearly established. Specific heats and refractive index are available only for the KCl–KBr system. With the exception of KCl–KBr, only one report is available for the dielectric constants of mixed crystals. The results on thermal expansion are too sparse; as a consequence, no information is available regarding the Gruneisen constant. Although the Debye–Waller factors have been determined for a few mixed crystal systems, the number of compositions studied in each system is too small. Third-order elastic constants have been predicted for NaCl–NaBr but experimental values are not available for any mixed crystal system. Phonon dispersion curves have been determined from neutron inelastic scattering experiments only for three mixed crystals, namely $K_{0.5}Rb_{0.5}I$ [97], $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ [98]. There is a lack of experimental data on the surface energy, thermal conductivity and magnetic susceptibility of mixed crystals.

Acknowledgements

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