

Lattice energy of mixed alkali halide crystals: Evaluation from sound velocity studies

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Based on single-crystal elastic constant data and employing Kudriavtsev's theory, which relates the lattice energy of the crystal U to the mean sound velocity u_m in the crystal, the lattice energies of NaCl-KCl, NaBr-KBr, KI-KBr and KCl-RbCl mixed crystals have been evaluated. In general, the lattice energies of these mixed crystal have been found to decrease with increase in the concentration of the second component. The present study highlights the application of Kudriavtsev's theory in predicting the lattice energies of mixed ionic crystals making use of sound velocity measurements.

Introduction

Crystalline state properties of ionic solids mainly depend upon the nature of the chemical bond between the ions and the interaction energies. The elastic constants and their pressure derivatives are indicative of the short range contributions to the cohesive energy. Lattice energy of ionic crystals is an important parameter which is directly connected to the binding forces in ionic solids and in turn to the elastic constants. Recently Subrahmanyam *et al.*¹⁻⁵ have applied Kudriavtsev's⁶ theory for the evaluation of lattice energies of a few ionic and mixed ionic crystals and the temperature dependence of lattice energy. The present work deals with the evaluation of lattice energy of mixed alkali halide crystals NaCl-KCl, NaBr-KBr, KI + KBr and KCl + RbCl using Kudriavtsev's⁶ theory and elastic constant data from literature.

A mixed crystal has properties analogous to those of the host crystals. The presence of a small impurity content might change the strength of the repulsive forces while maintaining the crystal symmetry. A survey of the literature⁷⁻¹⁰ shows that there are a few theoretical studies⁷⁻¹⁰ carried out on the static and elastic properties of mixed crystals. Argyriou and Howard¹¹ made an attempt to calculate the electrostatic potentials, Madelung constants and interaction energies in ionic crystals. Srinivasa Rao and Sanyal¹² studied the pressure induced structural phase transitions and elastic constants at high pressure for sodium halides using a model potential that

includes many body interactions due to electron shell overlap. Reddy and Suryanarayana¹³ observed a linear decrease in C_{11} with temperature and a steady increase in C_{44} with temperature in KCl- SrCl₂ mixed crystals. It is reasonable to expect that the variations taking place in the physical properties of pure and mixed ionic crystals with variation in temperature, pressure and chemical composition will depend on the lattice energy. In view of the above observations, it is of interest to evaluate the lattice energy of mixed alkali halide crystals from their elastic properties.

2 Theoretical Considerations

The sound velocity u_m is related to the lattice energy U of an ionic crystal, according to Kudriavtsev's theory⁶, by

$$M u_m^2 = \frac{\gamma n_1}{9} U \quad \dots(1)$$

where γ represents the ratio of specific heats which can be taken to be equal to unity and M represents the molecular weight of the crystal, n_1 is a constant which depends upon the lattice structure. The detailed derivation is given in earlier communications of the authors^{1,4}. Expressing M in kg mol⁻¹ and u_m in ms⁻¹ one can get U in J mol⁻¹, n_1 may take on values like 3, 5, 7, 9 and 10 depending upon the nature of bonding present in the crystals. For pure ionic crystals $n_1 = 5$ gives lattice

energy data in agreement with experimental data^{1,2} and hence $n_i = 5$ is taken in the present study to evaluate the lattice energy of mixed ionic crystals.

The crystals in the present study are cubic in nature. The mean sound velocity u_m is given by the relation

$$u_m = \left[\frac{1}{3} \left(\frac{1}{u_1^3} + \frac{2}{u_t^3} \right) \right]^{-1/3} \quad \dots(2)$$

The longitudinal and transverse wave velocities u_l and u_t of the polycrystalline aggregates of these cubic crystals can be evaluated from the single crystal elastic constant data using the Voigt-Reuss-Hill approximation¹⁴.

3 Results and Discussion

The mean sound velocities of the NaCl-KCl, NaBr-KBr, KI-KBr and KCl-RbCl mixed crystals have been evaluated making use of single crystal elastic constant data taken from literature¹⁵⁻¹⁷. To evaluate the sound velocities, the density data of the mixed crystals are necessary. For NaCl-KCl, NaBr-KBr, KI-KBr and KCl-RbCl mixed crystals, no such data are available in literature for concentrations for which the elastic constants are reported. The density values for the mixed systems of the present study have been evaluated using Vegard's law¹⁸, which predicts a linear composition dependence. The same procedure was followed by Nathan *et al.*¹⁹ for the case of KBr-KI system. Sirdeshmukh and Srinivas²⁰ have also outlined the utility by Vegard's law for the estimation of densities of mixed crystal systems. Barrett and Wallace²¹ have determined the densities of the NaCl-KCl system. For the NaCl-KCl system, the density value evaluated in the present work for a concentration of 89 mol % KCl in NaCl works out to $2.005 \times 10^3 \text{ kg m}^{-3}$. This value very well compares with the density value of $1.9964 \times 10^3 \text{ kg m}^{-3}$ reported by Barrett and Wallace²¹ for a concentration of 89.9 mol % KCl in NaCl. Similarly a density value of $2.034 \times 10^3 \text{ kg m}^{-3}$ is evaluated for a concentration of 73 mol % KCl in NaCl whereas the value given by Barrett and Wallace²¹ for 70 mol % KCl in NaCl is $2.0117 \times 10^3 \text{ kg m}^{-3}$. These two sets of values are in excellent agreement with the experimental values, the deviation being less than 1%. For KI-KBr system, the density data have been reported at different concentrations at which elastic data have been determined. The application of Vegard's law¹⁸ yields density data accurate to about 4% indicating a good agreement between experimental and predicted values of densities for mixed crystals.

The calculated values of lattice energy of NaCl-KCl, NaBr-KBr, KI-KBr and KCl-RbCl as a function of the mol % of the second component are shown graphically in Figs 1, 2, 3 and 4 respectively. The lattice energy values of these systems reported in literature are also included in the above figures for the sake of comparison.

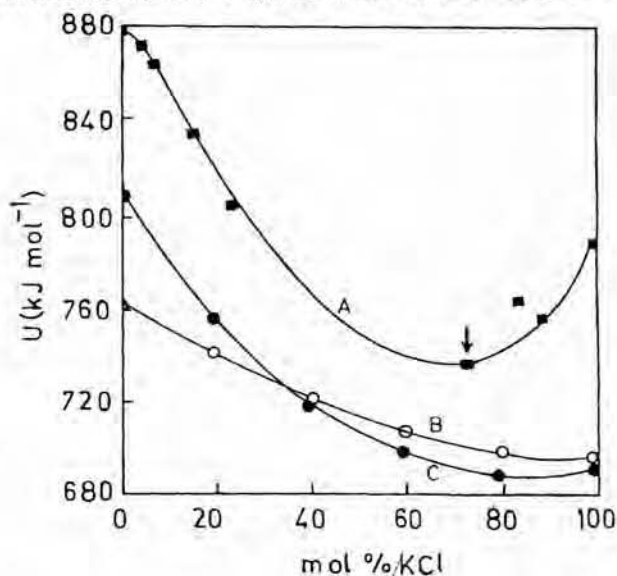


Fig. 1 — Variation of lattice energy (U) with mol% KCl of NaCl-KCl mixed crystal [(A) Present work, (B) Data evaluated by Belomestnyka *et al.*²² using Born's equation²³, (C) Data evaluated by Belomestnyka *et al.*²² using Nemilov's equation²⁴]

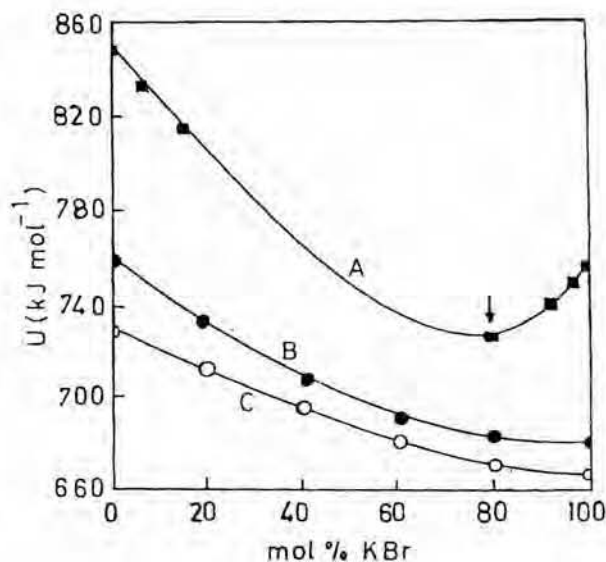


Fig. 2 — Variation of lattice energy (U) with mol % KBr of NaBr-KBr mixed crystal [(A) Present work, (B) Data evaluated by Belomestnyka *et al.*²² using Born's equation²³, (C) Data evaluated by Belomestnyka *et al.*²² using Nemilov's equation²⁴]

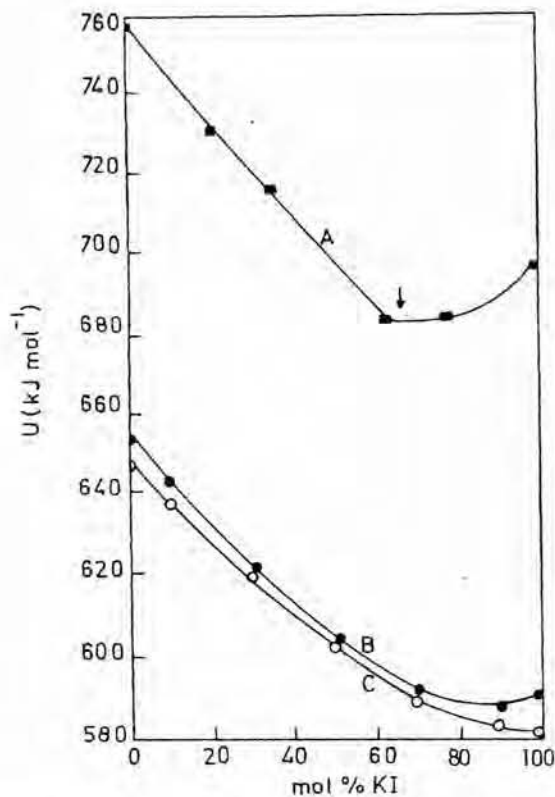


Fig. 3 — Variation of lattice energy (U) with mol % KI in KI-KBr mixed crystals [(A) Present work, (B) Data evaluated by Zavadvovskaya *et al.*²⁵ using theoretical values of r_0 , (C) Data evaluated by Zavadvovskaya *et al.*²⁵ using experimental values of r_0]

It is clear from Figs 1 and 2 that the lattice energy of NaCl-KCl and NaBr-KBr mixed crystals decreases non-linearly as the composition of the second component is increased. For these two mixed systems, the maximum negative deviation in the lattice energy with linear values occurs at 73 mol % of KCl in NaCl and 80 mol % of KBr in NaBr, respectively. Similar trend of variation of lattice energy with the increase in the concentration of the second component in these mixed crystals was reported by Belomestnykh and Sukhushin²². They have evaluated the lattice energies of these two mixed crystal systems using Born's²³ and Nemilov's²⁴ equations from single crystal elastic constant data. This negative deviation in the lattice energy from linear values may be attributed to the presence of defects in the lattice. The number of defects increases with the decreasing chemical stability of the mixed crystal.

As the concentration of the second component increases, the number of weakly bound ions in the lattice also increases thereby paving the way for the destabili-

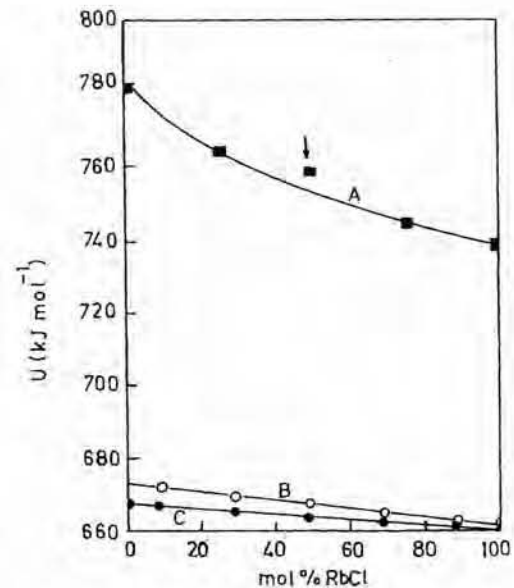


Fig. 4 — Variation of lattice energy (U) with mol % RbCl of KCl-RbCl mixed crystal [(A) Present work, (B) Data evaluated by Zavadvovskaya *et al.*²⁵ using theoretical values of r_0 , (C) Data evaluated by Zavadvovskaya *et al.*²⁵ using experimental values of r_0]

zation of the lattice. It is to be mentioned here that among the alkali halide mixed crystal systems, the NaCl-KCl system has the least stability and hence maximum deviation has taken place in the lattice energy values.

As can be seen from Fig. 3, the lattice energy of the system KI-KBr varies in a non-additive manner with composition. The maximum deviation in lattice energy occurs around 63 mol % of KI in KBr. This trend of variation is similar to the results given by Zavadvovskaya *et al.*²⁵ who have evaluated the lattice energy of KI-KBr mixed crystals on the basis of Durham and Hawkins method²⁶. In these calculation Zavadvovskaya used two different values for the equilibrium distance r_0 between neighbouring ions. These results are also presented in Fig. 3 for comparison.

For the KCl-RbCl mixed system, it is evident from Fig. 4 that the lattice energy decreases in a nonlinear manner with increase in the composition of RbCl-KCl. The maximum deviation from linear values of lattice energy in this system corresponds to an equimolar concentration of 50 mol % RbCl in KCl. This deviation from linear values increases with the decreasing resistance of the mixed crystal to decompose. Zavadvovskaya *et al.*²⁵ have also evaluated the lattice energy of the KCl-RbCl system using the Durham and Hawkins procedure²⁶. The results of the present work are similar to their studies.

As can be seen from Figs 3 and 4 the lattice energy data obtained in the present work are higher than the data reported in literature²⁵ for the systems KI-KBr and RbCl-KCl. It may be mentioned here that the lattice energy of mixed crystals has been determined only to a rough approximation in which no allowance has been made for the energy of the elastic distortion. Moreover, the lattice energy values calculated under the assumptions made by Zavadovskaya *et al.*²⁵ are incapable of explaining observed changes in the physical properties of mixed crystals with composition. In the present work, due to lack of density data of the mixed crystals for the concentrations at which elastic constants have been reported in literature, the authors have made use of Vegard's law¹⁸ for calculating the density of the mixed crystals. Any deviation of the density data calculated from the real values might affect the lattice energy data calculated. The deviations in the calculated lattice energy data of the present work with that of Zavadovskaya *et al.*²⁵ for the systems KI-KBr and RbCl-KCl may be attributed to the uncertainties involved in the input data.

The negative deviation in the lattice energy from linear values of these mixed crystals may be attributed to the presence of defects in the mixed crystal lattice. The number of defects increase with the decreasing chemical stability of the mixed crystal. As the concentration of the second component increases, the number of weakly bound ions in the lattice also increases thereby paving the way for destabilization of the lattice. Consequently, the lattice energy, depending on the composition of the mixed crystal, varies over the composition range with negative additivity. The deviation will be more for the least stable system and less for the most stable system. The behaviour indicates the weakening of the binding forces between the ions in the mixed crystal lattice compared with the lattice of the host crystal.

In an earlier paper¹, the authors have reported the variation of lattice energy of NaCl-NaBr, KCl-KBr and AgCl-AgBr mixed crystals. In the present work, studies are made on the NaCl-KCl, NaBr-KBr, KI-KBr and KCl-RbCl mixed systems. From both the studies it can be concluded that the variation in the lattice energy as a function of composition is more or less the same whether one has a cation or an anion impurity. In general, the composition dependence of lattice energy is highly non-linear. This was also emphasized by Sirdeshmukh and Srinivas¹⁹ in their review of the physical properties of alkali halide mixed crystals.

4 Conclusions

The results of the present work highlight the application of Kudriavtsev's⁶ theory in estimating the lattice energies of mixed crystals, making use of ultrasonic velocity data. In view of the fact that the experimental data on the lattice energies of mixed ionic crystals are sparse, the present study becomes useful and significant.

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