ELASTIC PROPERTIES OF Na$_x$K$_{1-x}$Br AND Na$_x$K$_{1-x}$Cl SOLID SOLUTIONS

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A pulsed ultrasonic method has been used to measure the speeds of longitudinal and transverse elastic waves along [100] and [110] in single crystals of Na$_x$K$_{1-x}$Br and Na$_x$K$_{1-x}$Cl solid solutions in the range 20-180°C; the elastic constants $c_{ij}$ have been determined. These values have been extrapolated to 0°C, while the bulk modulus and shear modulus have been calculated.

We have previously [1, 2] determined the adiabatic elastic constant $c_{1k}$, as well as Young's modulus and the shear modulus for KBr$_x$Cl$_{1-x}$ and KBr$_x$I$_{1-x}$ solid solutions; the negative deviation from additivity is greater in the second system, which agrees with the conclusions of [3] on the behavior of the elastic moduli of solid solutions and compounds formed with absorption of heat.

Here we report the elastic properties Na$_x$K$_{1-x}$Br and Na$_x$K$_{1-x}$Cl solid solutions; these results can be used in conjunction with measurements of the specific heat, thermal expansion, and so on to construct a thermodynamic theory of mixed crystals. The elastic properties in a system of solid solutions enable one to explain the variations within the system, and also from one system to another, while also enabling one to check existing theories for $c_{1k}$, as well as predicting and adjusting the elastic characteristics of required compositions.

The solid solution single crystals were grown from the melt by the Kyropoulos method; the specimens were free from visible contamination and cracks, and were cut as parallelepipeds of long edge of length 12-20 mm. Mechanical processing and chemical polishing were used to render the faces parallel to 8.10$^{-4}$. We used a standard instrument type UZIS [4] at 1.67 MHz to measure the speeds of longitudinal and transverse elastic waves along the [100] and [110] directions, the measuring line in this instrument being adapted for measurement over the range from room temperature to +180°C. X-ray methods were used to determine the composition and the orientation of the crystallographic direction.

The elastic constants were calculated from the speed measurements via the usual relationships for cubic crystals [5]. The densities needed to calculate the $c_{1k}$ were measured by weighing in liquids to ±0.001 g/cm$^3$. The temperature dependence of the speeds was processed by least squares; the coefficients of variation for the constants were $c_{44}$ 1.2%, $c_{11}$ 1.8%, $(c_{11} - c_{12})/2$ 1.5%.

Figures 1-3 give the results; the elastic constants as functions of temperature show a linear trend, which is characteristic of many solid substances, and applies in particular to the alkali halides [6-8]. The temperature coefficients of the $c_{1k}$ show additivity in relation to the composition; however, the elastic constants themselves deviate in a negative sense from additivity, the maximum occurring at 45-50 mole % NaBr in KBr or NaCl in KCl, while the relative magnitude of the effect increased with temperature. The equilibrium composition gave a $\Delta c_{11}/c_{11}$ at room temperature of 15.5% for Na$_x$K$_{1-x}$Br and 13.2% for Na$_x$K$_{1-x}$Cl, while the $\Delta c_{44}/c_{44}$ were, respectively, 10.0 and 6.0%. Then the deviation from additivity for Na$_x$K$_{1-x}$Cl is greater than that for Na$_x$K$_{1-x}$Br, which correlates with the stability of these systems and the heats of formation, the latter being larger by a factor of 1.3 for the first system [9]. Our results for $c_{12}$ also indicate a negative deviation from additivity, but the large error in measuring it does not allow of any final conclusion on the composition dependence.


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The results on the concentration dependence indicate a general weakening of the ion binding forces relative to the components. This is clear also from the melting-point diagram [10]. The minimum melting point occurs at the equimolecular position, and the deviation from linear relationship is 19.7% for Na_xK_{1-x}Cl and 14.3% for Na_xK_{1-x}Br.

A lattice theory of alkali halides has been developed [9, 11] via the defect model of [12]; the following symmetrical formula has been given [11] for the deviation of c_{11}:

\[ \Delta c_{11}(x) = 3Dx \left(1 - x\right) \]

where

\[ D = \frac{\left[(K_1V_x)^2 - (K_2V_x)^2\right](K_2 - K_1)}{2K_1K_2V_1V_x} \] (1)

is expressed in terms of the bulk modulus K_1 and the volumes of the unit cells of the component, while x is concentration (K_2 < K_1).

Figure 4 shows the calculated values of \( \Delta c_{11} \) given by this formula for four solid-solution systems, together with the observed deviations at room temperature; (1) describes well the deviation of c_{11} only for KCl_{1-\text{x}}Br\_\text{x}, where the deviation is comparatively small. In the case of the other systems, the calculated c_{11} are less than the observed ones. On the qualitative side, theory and experiment give a parabolic concentration dependence, and this type of relation for c_{11} and Young's modulus has been observed for some alloys [13].

The anisotropy factor 2c_{44}/c_{11} - c_{12} and the Cauchy relation c_{44} = c_{12} show also negative deviation from additivity as a function of composition; the equation c_{44} = c_{12} implies spherical symmetry in the charge distribution and in the interaction between the ions. If it is obeyed, one can use theoretical expressions for the elastic constants as in [14], which have been derived from the Born–Mayer potential,