ON THE VALIDITY OF IOSILEVSKII RELATION IN SOME BINARY ALKALI HALIDE SOLID SOLUTIONS

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It is found that the approximative Iosilevskii relation in calculating the Debye frequency for binary alkali halide solid solutions is valid within a few per cent in some binary mixed crystals.

In calculating the lattice heat capacity at low temperatures for substitutional solid solutions Iosilevskii [1] has presented a linear relationship for the Debye frequency ν_D based on the isotopic approximation

$$\nu_D^{-2} = \sum_i \nu_{iD}^{-2} \cdot x_i, \tag{1}$$

where ν_{iD} and x_i are the Debye frequency and the mole fraction, respectively, of the pure component i. By using the approximation of mutually independent frequencies ν_{iD} in a binary alkali halide solid solution and noting the relation between ν_D and the corresponding wavelength λ_D we have

$$\nu_D^{-2} \propto \lambda_D^2 = f(x, \lambda_{1D}, \lambda_{2D}), \tag{2}$$

where $f(x, \lambda_{1D}, \lambda_{2D})$, calculated from experimental results, is a function of mole fraction x with parameters λ_{1D} and λ_{2D} of the pure components. Kamiyoshi and Nigara [2] have given a semi-empirical expression based on Clausius-Mosotti's and Lorentz-Lorentz's equations for calculation of the dielectric constant of mixed alkali halide crystals, from which the following expression is directly derived

$$\lambda_D^2 = [B - x_1 A_1 (l_1/l)^3 - x_2 A_2 (l_2/l)^3]/[x_1 (B_1 - A_1)(l_1/l)^6 \lambda_{1D}^{-2} + x_2 (B_2 - A_2)(l_2/l)^6 \lambda_{2D}^{-2}], \tag{3}$$

with the notations

$$A_i = (R_i^2 - 1)/(R_i^2 + 2),\ B_i = (\varepsilon_i - 1)/(\varepsilon_i + 2),\ B = (\varepsilon - 1)/(\varepsilon + 2);$$

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ε and ε_i are the measured dielectric constants of the mixed crystal and pure components, R_i values of refractive index [2, 4], l and l_i the lattice constants of solid solution and components, and x_i the mole fraction of the component i and λ_{iD} the wavelength of averaged infrared absorption spectrum shifted to either side of the maximum value peak. For calculating λ_{iD} from the main resonance wavelength [2–4] λ_{i0} and the anharmonicity factor [3] $b = \lambda_d/\lambda_c$ the following estimation was used

$$\lambda_{iD} = b\lambda_{i0}. \tag{4}$$

For the lattice constant in mixed crystals a second order equation was used based on experimental [5–7] X-ray diffraction measurements

$$l = x_1 l_1 + x_2 l_2 + 4dx_1 x_2, \tag{5}$$

where d is a positive factor representing the deviation of equimolar solid solution from Vegard's rule. Numerical values used are given in Table I and II.

TABLE I

Numerical values used in the calculation of averaged wavelength λ

	1	2	3	4	5	6
Crystal	ε	l(Å)	R^2	$\lambda_0(\mu m)$	b	$\theta_D(\mu m)$
NaCl	5.93	5.6402	2.25	61.1	0.96	58.5
NaBr	6.34	5.9772	2.62	74.6	0.97	72.5
KCl	4.80	6.2931	2.13	70.7	1.03	73
KBr	4.87	6.5966	2.33	88.3	1.03	91
KI	5.12	7.0655	2.69	102.0	1.06	107
RbCl	4.94	6.5810	2.19	84.8	1.06	90
RbBr	4.85	6.889	2.33	114.0	1.09	124
RbI	4.83	7.342	2.63	129.5	1.11	145

[1] Columns 1–4 are taken from Ref. [1], b calculated with the aid of values from Ref. [3].

TABLE II

Square of averaged wavelength λ_D as a function of mole fraction

	Na(Cl, Br)		K(Cl, Br)		Rb(Cl, Br)		(K, Rb)Cl		(K, Rb)I	
x	ε	λ_D^2	ε	λ_D^2	ε	λ_D^2	ε	λ_D^2	ε	λ_D^2
0	5.93	3422	4.80	5929	4.94	8100	4.80	5329	5.12	11449
0.1	6.015	3597	4.84	5602	4.965	8665	4.835	5603	5.12	12242
0.3	6.17	3965	4.905	6176	4.995	9893	4.89	6158	5.105	13946
0.5	6.26	4327	4.94	6773	5.005	11282	4.93	6723	5.055	15758
0.7	6.33	4705	4.935	7372	4.99	12852	4.955	7293	4.98	17719
0.9	6.345	5073	4.895	7972	4.905	14490	4.955	7844	4.88	19841
1.0	6.34	5256	4.87	8281	4.85	15376	4.94	8100	4.83	21025
	$4d \sim 0.032$ Å		$4d \sim 0.019$ Å		$4d \sim 0.044$ Å		$4d \sim 0.04$ Å		$4d \sim 0.036$ Å[1]	

[1] Estimated. Values of ε are taken from Ref. [2]; λ_D^2 is given in $(\mu m)^2$.

In Table III some deviations from the v^{-2} and v^{-1} linearities are calculated by the means of data taken from Table II with the notation $\Delta\lambda_D^n = \lambda_D^n\,(x = 0.5) - 0.5[\lambda_D^n(x = 0) + \lambda_D^n(x = 1)]$. In Tables II and III the value $x = 1$ of the mole fraction refers to the component having greater lattice constant.

TABLE III

Calculated relative deviations from the Iosilevskii and linear-λ relations

	$\Delta\lambda_D^2/\lambda_D^2(0.5)\%$	$\Delta\lambda_D/\lambda_D(0.5)\%$
Na(Cl, Br)	−0.3	+0.4
K(Cl, Br)	−0.1	+0.4
Rb(Cl, Br)	−4.0	−0.7
(K, Rb)Cl	+0.1	+0.6
(K, Rb)I	−3.0	−0.4

It is seen from Table III that for systems Na(Cl, Br), K(Cl, Br) and (K, Rb)Cl the calculated v^{-2} linearity is somewhat better than the linear-λ rule. Experimental results reported by Mitsuishi [8], Karlsson [9] and Milnes and Wallace [10] indicates that the infrared absorption wavelength for the systems K(Cl, Br) and (K, Rb)Cl vary linearly with the mole fraction [8] at 300°K and that the Debye temperatures calculated for the K(Cl, Br) mixed crystal from the specific heat measurements at low temperatures [9] and even up to room temperature [10] obey the Iosilevskii approximation, which can also be verified from X-ray intensity measurements within experimental error, done by Ahtee *et al.* [11] by using the theory of Valvoda and Synecek [12] for the Debye temperature θ_D. The deviations of θ_D from Vegard's rule compared with the pure components are by about 50% larger calculated with the aid of experimental elastic constant data according to Fancher and Barsch [13] than the one found with Iosilevskii relation at room temperature for a family of alkali halide solid solutions, which would give for the exponent in the v^{-n} relation a value $n > 2$. Taking into account that Fancher and Barsch used a linear approximation for the volume and elastic constants in solid solutions and the fact that the absolute deviations are small, the exponent value $n = 2$ will be in order. It should be noted, anyhow, that the reports on infrared reflectivity in some alkali halide solid solutions [3, 14, 15] giving nearly linear curves of the wavenumber for the $L0$ and $T0$ modes at constant temperature and pressure and even a two-component spectra for the (K, Rb)I mixed crystal imply that a more detailed study of the infrared absorption spectra in binary alkali halide solid solutions is necessary.

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