

VACANCIES AND CHANGES IN THE SOUND VELOCITY IN ALKALI HALIDES ON PASSING THROUGH THE MELTING POINT

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ABSTRACT

Basing on the vacancy model of melting, proposed previously by the authors an expression for the ratio of the sound velocity (Debye averages) in the solid U_s and liquid U_l phases of alkali halides, at their melting points, has been derived. The calculated value of the U_s/U_l ratio equal to 1,23 (the same for all the alkali halides) satisfactorily agrees with the experimental data available in the literature for 13 alkali halides.

INTRODUCTION

Knowledge of the propagation constants for sound waves is often of great value in the study of the structure of condensed matter. The application of the ultrasonic wave method to the experimental investigations of the solid and liquid phases near the melting point, and during the melting process, may be of special interest by bringing us more knowledge about the mechanism and kinetics of this universal, but poorly understood, phenomenon. However, because of the difficult problems encountered in the realization of measurements, experimental data on the changes in the sound propagation constants on passing through the melting point are rather scarce. Nevertheless, the experimental data available in the literature can be used for checking the reliability of the predictions of the existing theories and models of the melting process. The purpose of the present study was to compare the changes in the velocity of sound propagation in alkali halides on passing through the melting point, predicted by the vacancy model of melting [1-5], with the available experimental data [6-18].

CALCULATION OF THE U_s/U_L RATIO FROM THE VACANCY MODEL OF MELTING

In a series of papers [1-5] the existence of correlations between the changes of various physical properties of alkali halides at the melting point, and changes of the same properties due to the creation of vacancies, has been revealed. On the basis of these correlations a vacancy model of melting has been proposed, according to which:

1. Melting starts when the concentration of Schottky defects in a solid phase reaches a critical value of 0.0017 (mole fraction), and

2. The melting process is a process of creation of additional vacancies at the expense of the heat of melting. The increase of the concentration of Schottky defects during the melting of alkali halides is approximately equal to $\Delta c \approx 0.15$.

The model, having its roots in Frenkel's [19] hole theory of liquids and the vacancy model of melting of metals and rare gas solids [21, 22], permits the prediction, in a good quantitative agreement with experimental data, of the changes in many of the physical properties of alkali halides (e.g. entropy, surface tension thermal expansion coefficient, heat capacity, coordination number and the first coordination sphere radius, etc.) due to the melting process. According to the proposed vacancy of model of the melting process, the concentration of vacancies in the liquid phase of alkali halides is approximately 100 times larger than that in the solid state at the melting point. Thus, the liquid phase could be treated, to the first approximation, as a strongly defected, highly disordered solid, and consequently all the changes in the physical properties occurring on passing through the melting point can be explained as the result of an increase in the vacancy concentration. The last statement should also apply to the experimentally observed jump in the velocity of sound propagation.

The average Debye velocity of propagation of sound waves in an isotropic homogenous is related to the Debye temperature θ and the molar volume V according to the formula:

$$U = k \theta \sqrt[3]{V} \quad (1)$$

where k is the proportionality factor (constant).

Consequently, for the solid and liquid phases at the melting point we can write:

$$U_s = k \theta_s \sqrt[3]{V_s} \quad (2)$$

and

$$U_l = k \theta_l \sqrt[3]{V_l} \quad (3)$$

where the subscripts s and l denote the solid and the liquid phases, respectively. From eqs. (2) and (3) it follows trivially that

$$\frac{U_s}{U_l} = \frac{\theta_s \sqrt[3]{V_s}}{\theta_l \sqrt[3]{V_l}} \quad (4)$$

The effect of various point defects on the phonon spectrum of crystals belongs to the fundamental problems of solid state physics. There have been many efforts by various authors to find a method to describe the effect of different point defects on the measurable characteristics of the vibrational spectrum of crystals (e.g. the Debye temperature), but because of the complexity of the problem, the solutions are only approximate, and therefore of limited value [22-24]. The simplest (and most convenient for our purposes) form of the relation describing the dependence of the Debye temperature upon vacancy concentration in crystal has been derived by Masharov [23]:

$$\theta_v = \theta_0(1 - 1.5 \cdot C_v) \quad (5)$$

where θ_0 is the Debye temperature for an ideal, defect-free crystal, θ_v is the Debye temperature for a crystal containing vacancies and C_v denotes concentration (mole fraction) of the vacancies.

According to the two postulates of the vacancy model of melting, the solid phase at the melting point can be treated as a nearly perfect crystal in comparison with the liquid phase, which in turn could be treated as a strongly defected crystal. Thus, making use of eq. (5) we can write

$$\theta_l \cong \theta_s(1 - 1.5 \cdot \Delta C_v) \quad (6)$$

and, in accordance with the second postulate of the vacancy model melting,

$$\frac{\theta_l}{\theta_s} \cong 0.775 \quad (7)$$

The change in the volume of alkali halides on melting may also be interpreted as the result of the formation of additional vacancies during the melting process. It is known that the formation of a single Schottky pair in alkali halides causes an increase of the crystal volume by 1,1 of the molecular volume [1]. Therefore the relative change in the volume of alkali halides due to the melting process may be expressed by

$$\frac{\Delta V}{V_s} \cong 1.1 \cdot \Delta C_v \cong 0.165 \quad (8)$$

which agrees well with the experimental data [1]. Consequently

$$\frac{V_l}{V_s} \cong 1.165 \quad (9)$$

Combining eqs. (4), (7) and (9) one obtains, finally, a simple relation between the values of the velocity of sound propagation in the solid and liquid phase of alkali halides at the melting point

$$\frac{U_s}{U_l} \cong 1.23 \quad (10)$$

COMPARISON OF THE CALCULATED U_s/U_l VALUE WITH EXPERIMENTAL DATA AND CONCLUSIONS

Inspection of the available literature on the experimental investigations of the temperature dependence of the velocity of sound in alkali halides revealed that there are no reports on measurements carried out under the same conditions for both the liquid and solid phases, or in the process of melting and/or solidification.

Values of the sound velocity in the liquid phase just above the melting point have been very accurately measured for all the alkali halides, but similar data for the solid phase just below the melting point are lacking. There are, however some papers [6, 12-18] reporting the values of the elastic constants c_{11} , c_{12} and c_{44} of alkali halides measured at temperatures close to the melting point. Availability of these data permits to calculate the velocities of the longitudinal, u_l and transversal, u_t , sound waves at the melting point according to the relations:

$$u_l = \sqrt{\frac{c_{11} + c_{12} + 2c_{44}}{2\rho}}; \quad u_t = \sqrt{\frac{c_{44}}{\rho}} \quad (11)$$

where ρ is the density of the solid phase at the melting temperature.

Using the u_l and u_t values determined from the elastic constants, the Debye average sound velocity U_s in the solid phase at the melting point has been calculated according to the formula:

$$\frac{3}{U_s^3} = \frac{1}{u_l^3} + \frac{2}{u_t^3} \quad (12)$$

These values were used for calculating the values of the U_s/U_l ratio for individual salts. The results of these calculations are given in Table I. The sources of the U_s and U_l values used are also indicated.

Table 1.

	c_{11}	c_{12}	c_{44}	U_s	U_l	$\frac{U_s}{U_l}$
	10^{10} [Pa]			[m/s]		
	1.99	1.21	0.95	2534 [13]	1756 [8]	1.44
KCl	1.46	0.73	0.54	1935 [14]	1577 [9]	1.23
RbCl	1.11	0.40	0.39	1363 [15]	1280 [10]	1.06
NaF	4.53	1.01	2.16	3070 [6]	2082 [10]	1.61
KF	2.30	2.04	1.00	2358 [13]	1833 [11]	1.29
RbF	2.47	1.50	0.83	1731 [16]	1380 [11]	1.25
NaBr	1.08	1.24	0.70	1768 [17]	1340 [11]	1.32
KBr	1.51	0.62	0.48	1539 [12]	1273 [11]	1.21
RbBr	1.32	0.40	0.30	1094 [12]	1112 [7]	0.98
Lil	1.36	1.10	1.06	1865 [13]	1232 [11]	1.51
Nal	1.39	0.68	0.59	1507 [12]	1144 [10]	1.32
KI	1.07	0.63	0.33	1199 [12]	1116 [10]	1.07
Rbi	1.07	0.60	0.25	969 [18]	1004 [11]	0.97

Experimental data on the values of the elastic constants of alkali halides (c_{11} , c_{12} , c_{44}) average Debye sound velocities in the solid (U_s) and liquid (U_l) phases of alkali halides at their melting points, and the U_s/U_l ratio.

As it is seen from Table I. the values of the U_s/U_l ratio for individual salts, ranging from 0.97 for RbI to 1.61 for NaF, are very close to the value of 1.23 predicted on the basis of the vacancy model of melting. The mean value of U_s/U_l ratio for 13 alkali halides listed in Table I amounts 1.25 with a relative standard deviation of 15 %. This agreement between the experimental data and the value of the U_s/U_l ratio calculated in the present study corroborates the validity of the vacancy model of melting.

It must be noted however that Masharov's relation (5) used for derivation of eq. (10). has been obtained under the assumption that the vacancies are uniformly distributed and do not interact among themselves. This assumption may be valid only for relatively small vacancy concentrations, and is certainly not fulfilled in the case of liquid alkali halides in which, according to the second postulate of the vacancy model of melting, the vacancy concentration (mole fraction) is of the order of 0.15. The possible effect of the mutual interaction of vacancies at large concentrations on the Debye temperature and thus on the U_s/U_l ratio for metals deserves further study.

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