Density of Crystalline Alkali Chlorides and Their Eutectic Mixtures Near the Melting Point

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The density of crystalline alkali chlorides and their eutectic mixtures near their melting point was first measured with the modified Archimedes's method. The premelting effect found was ascribed to the peculiarities of defects in the crystal lattice before melting. The molar volume and concentration of cooperative defects were calculated with the experimental data obtained.

Introduction

Today there is a great body of experimental data on the temperature dependencies of different physical and chemical properties of ionic compounds near their melting point. Ubbelohde[1] and Heyes[2] pointed out that in some temperature intervals before the phase transition of salts with lattice and chain structures (glass) and fluorite-like crystals (say, CaF_2, PbF_2, $SrCl_2$, UO_2) the premelting effects related to the local disordering of structure can be observed, which results in an unusual change of properties, such as density, electrical conductivity, and heat capacity. In all such cases the premelting effects are typically referred to the destruction of the anion sublattice. For alkali halides, those having the rock salt structure of cation and anion sublattices are practically identical, and premelting effects can hardly be expected. However, according to X-ray analysis data[3,4] the lattice parameter of alkali halides deviate**s** from the expected linear temperature dependence near the melting point. Previous work[5] has stated the small reduction of compressibility of NaCl, 7° prior to its melting. By studying the thermal conductivity and thermal diffusivity of many alkali halides and their eutectic mixtures,[6,7] the nonlinear behavior of these properties with a minimum in the temperature range of (20 to 40) K before the phase transition was found. The data obtained for sound propagation in these crystalline salts[8,9] also showed the unusual character of temperature dependence near the melting point. All of the above-mentioned results of the experiments show the "irregular" variation of different properties of ionic compounds in the temperature range just before melting. However, the question is far from being completely studied. Accordingly, it is necessary to develop new methods and approaches to accomplish our knowledge of the basic causes of premelting phenomena.

In present report the results of density measurements and calculated magnitudes of the molar volume of alkali chlorides and their eutectic mixtures in solid phase near the melting point are given and discussed.

Experimental Section

To measure the density of crystal substances over a wide temperature range, we developed an original device based on the Archimedes's method.[10] Metallic gallium (T_{melt} = 302.8 K)

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was selected as a working liquid due to its low volatility up to 1700 K. The solid salts under study were placed inside a tungsten bell to avoid their emerging. A hole was drilled at the top of the bell to remove adsorbed gas during evacuation. The measuring procedure had two stages: at first, the tungsten bell was weighed over the range of working temperatures, and then the measurements were made for the suspended system with the salt sample. The measuring error did not exceed ± 0.5 %.

The salts for the experiments were prepared using the method of multiple zonal recrystallizations.

The density (ρ) of the crystalline salt at given temperatures was calculated by the following equation:

$$\rho = m/(V_S - V_0) \tag{1}$$

where m is the salt sample mass and V_S and V_0 are the volumes of the suspended system with and without the salt sample, respectively.

Results and Discussion

The temperature dependencies of the density of crystalline NaCl (T_{melt} = 1073 K), KCl (T_{melt} = 1043 K), RbCl (T_{melt} = 992 K), and CsCl (T_{melt} = 919 K) as well as 0.605 LiCl + 0.395 CsCl (T_{melt} = 598 K) and 0.585 LiCl + 0.415 KCl (T_{melt} = 628 K) eutectic mixtures are shown in Table 1.

We also measured the density of solid KCl and NaCl using the γ-radiation method.[11] The same temperature dependencies were observed with the density magnitudes only 1 % higher compared to results presented here. It confirms the high reliability of the presented data.

Using the experimental values of density, the molar volumes of the solid alkali chlorides under study were calculated. At the melting point the molar volume of alkali chlorides increases sharply to its value inherent in molten salts.[12] The relative changes of molar volume at the phase transition calculated by us are in a good agreement with the data,[1] as can be seen in Table 2.

The "unusual" temperature dependence of the density shown in Figure 1 and other properties (thermal conductivity, thermal diffusivity, sound velocity)[6−9] of crystalline alkali halides and their eutectic mixtures found near the phase transition temperature can be explained with the assumption of irregular distribution of thermal and doped defects in the crystal lattice. One can suppose that their interaction results in the appearance

Table 1. Experimental Density of Crystalline NaCl, KCl, RbCl, CsCl, 0.605 LiCl + 0.395 CsCl, and 0.585 LiCl + 0.415 KCl as a Function of Temperature

NaCl		KCl		RbCl		CsCl		0.585 LiCl + 0.415 KCl		0.605 LiCl + 0.395 CsCl	
T_{melt} = 1073 K		T_{melt} = 1043 K		T_{melt} = 992 K		T_{melt} = 919 K		T_{melt} = 628 K		T_{melt} = 598 K	
T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
1013	1931.2	973	1805.8	903	2578.4	843	3074.5	568	1972.4	523	2681.2
1023	1905.8	983	1803.6	913	2573.5	853	3067.6	573	1968.8	528	2679.1
1033	1890.4	993	1800.6	923	2567.8	863	3060.2	578	1966.1	533	2676.4
1043	1888.3	1003	1797.1	933	2562.2	873	3052.4	583	1964.2	538	2672.7
1053	1882.0	1013	1794.5	943	2556.1	883	3046.0	588	1964.1	543	2669.5
1063	1884.9	1023	1793.6	953	2551.7	893	3040.9	593	1965.2	548	2666.8
1073	1889.8	1033	1793.6	963	2548.6	903	3039.5	598	1967.7	553	2663.6
		1043	1796.6	973	2547.6	913	3041.8	603	1970.1	558	2661.3
				983	2550.3			608	1972.1	563	2659.9
				993	2556.4			613	1973.7	568	2659.5
										573	2660.0
										578	2661.4
										583	2663.7
										588	2667.5
										593	2672.2
										598	2678.3

Figure 1. Density of crystalline ●, NaCl; ○, KCl; □, RbCl; ■, CsCl; ▲, 0.585 LiCl + 0.415 KCl; and △, 0.605 LiCl + 0.395 CsCl near the melting point.

Table 2. Relative Changes of Alkali Chloride Molar Volume at the Melting Point

| salt	T_{melt} K	V_{melt}[a] $kg \cdot m^{-3}$	V_{cryst} $kg \cdot m^{-3}$	$\Delta V/V_{cryst}$	$\Delta V/V_{cryst}$[b]
NaCl	1073	37740	30920	0.220	0.250
KCl	1043	48870	41490	0.178	0.173
RbCl	992	53930	47400	0.138	0.143
CsCl	919	60110	55300	0.087	0.105

[a] Ref 12. [b] Ref 1.

of many-particle clusters (cooperative defects)[1,13] which leads to closer ion packing in the crystal lattice. Using the experimental data on densities or molar volumes, it is possible to estimate the relative quantity (fraction) of cooperative defects N in crystalline alkali halides. The fraction of cooperative defects is equal to the ratio of the difference between the value of idealized molar volume of the salt crystal without cooperative defects (V_{id}), and the experimental value (V_{exp}) at the given temperature to its magnitude determined at the melting temperature:

$$N = (V_{id} - V_{exp})_T/(V_{id} - V_{exp})_{Tmelt} \qquad (2)$$

From Figure 2, where the temperature dependence of the molar volume of crystalline cesium chloride is presented as an example, one can see the procedure of estimating the relative quantity of cooperative defects.

The fraction of cooperative defects increases as the melting point is approached (see Figure 3) and was used to appreciate other properties (thermal conductivity, sound velocity), which
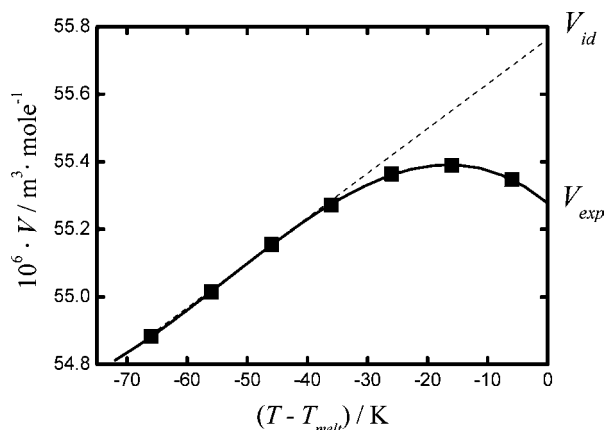
Figure 2. Variation of V_{id} (dotted line) and V_{exp} (solid line) of crystalline CsCl near the melting point.
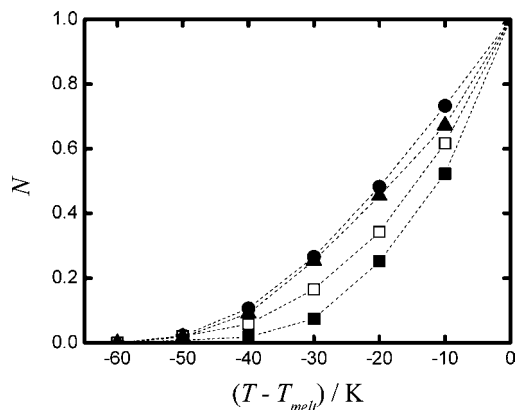
Figure 3. Fraction of cooperative defects (N) in alkali chloride crystals: ●, NaCl; ▲, 0.585 LiCl + 0.415 KCl; □, RbCl; and ■, CsCl.
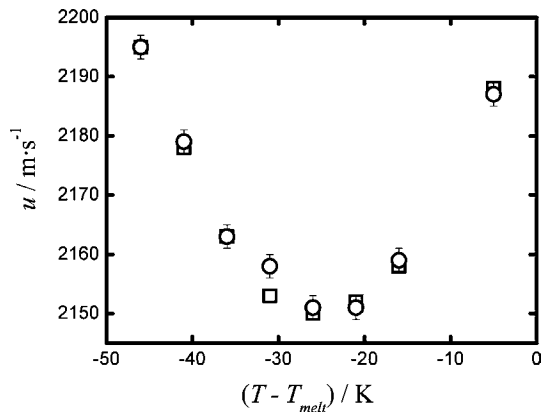
Figure 4. Comparison of the ○, experimental, and □, calculated values of sound velocity u in crystalline CsCl near the melting point.
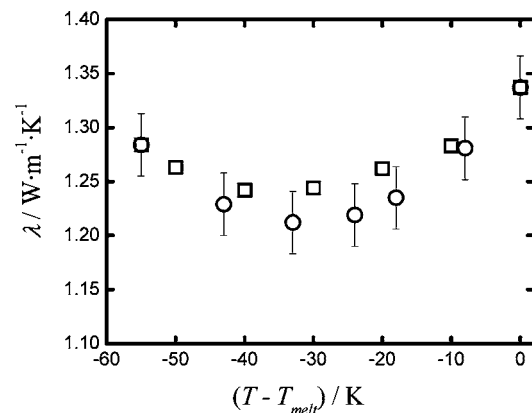
Figure 5. Comparison of the ○, experimental, and □, calculated values of thermal conductivity λ of crystalline (0.585 LiCl + 0.415 KCl) eutectic mixture near the melting point.

also have "unusual" temperature dependences near the phase transition temperature.[6-9]

Calculations were made using the following formula:

$$A_{exp} = A_{id} + \Delta A_{def} \qquad (3)$$

where A_{exp} is the experimental value of a property, A_{id} is the property value of the idealized crystal without cooperative defects (it is determined in the same way as V_{id}), and $\Delta A_{def} = N (A_{exp} - A_{id})_{Tmelt}$ is the "excess" value of the property that depends on the fraction of cooperative defects N. As evident from the figures above, illustrating the properties of cesium chloride and (0.585 LiCl + 0.415 KCl) eutectic mixture as examples, the experimental and predicted values of sound velocity u (Figure 4) and thermal conductivity λ (Figure 5) are in good agreement.

Conclusions

The adapted method of hydrostatic weighing was used to measure the density of crystalline alkali chlorides and their eutectic mixtures close to the melting point. The unusual change of the density with the temperature was found, which can be explained by interaction of defects of the crystalline lattice resulting in formation of cooperative defects. Their relative quantity was calculated and used for estimation of sound velocity and thermal conductivity of typical ionic crystals near the melting point.

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