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A VIEW AND A REVIEW OF THE MELTING OF ALKALI METAL HALIDE CRYSTALS

Part 1. A melt model based on density and energy changes

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Although melting is a most familiar physical phenomenon, the nature of the structural changes that occur when crystals melt are not known in detail. The present article considers the structural implications of the changes in physical properties that occur at the melting points, T_m, of the alkali halides. This group of solids was selected for comparative examination because the simple crystal lattices are similar and reliable data are available for this physical change. For most of these salts, the theoretical lattice energies for alternative, regular ionic packing in 4:4, 6:6 and 8:8 coordination arrangements are comparable. Density differences between each solid and liquid at T_m are small. To explain the pattern of quantitative results, it is suggested that the melt is composed of numerous small domains, within each of which the ions form regular (crystal-type) structures (regliq). The liquid is portrayed as an assemblage of such domains representing more than a single coordination structure and between which dynamic equilibria maintain continual and rapid transfers of ions. T_m is identified as the temperature at which more than a single (regular) structure can coexist. The interdomain (imperfect and constantly rearranging) material (irregliq) cannot withstand shear, giving the melt its fluid, flow properties. From the physical evidence, it is demonstrated that the structural changes on melting are small: these can accommodate only minor modifications of the dispositions of all, or most, ions or larger changes for only a small fraction. This proposed representation, the set/liq melt model, may have wider applicability.

Keywords: *alkali halide, fusion, melting, melting point, melt structure*

Introduction

Perhaps the most frequently observed, and obvious, consequence of heating a crystal is that it melts: this generalization summarizes the experience gained through innumerable observations for countless solids. For a majority of pure crystalline substances there is a characteristic (precise) temperature, the melting point (T_m), at which the long range order of the crystal lattice is lost, together with its ability to withstand a shearing force. Many and varied exceptions to this generalization are known, including solids that sublime and/or decompose chemically before liquefaction, other crystals undergo a progressive, stepwise loss of order (through liquid crystals) and there are substances that exhibit some solid-like of properties, such as glasses. Nevertheless, experience identifies fusion at T_m as an important and widespread discontinuous change, usually sharp, in the properties of materials, a consequence of the accommodation of heat energy. Melting is a characteristic step in the sequence of transformations from the regular, sometimes approaching perfect, crystal at low temperature, where constituents are effectively immobilized, to the almost freely moving molecules, atoms or ions of a gas at high temperature and low pressure. Progressive acquisition of thermal energy systematically eliminates all regular structure and order: melting is a significant step in this heat-induced progress towards disorder.

Structural and bonding features of innumerable individual crystalline phases have been characterized, in greater or in lesser detail, including identifications of the various regular dispositions of atoms within lattice arrays, their interactions, thermal motions and the types of imperfections and impurities that may be present. Theoretical explanations, often based on structural and bonding concepts, have been developed to account for the physical and chemical properties of pure crystals and of solid mixtures of diverse types. However, the specific processes that characterize the transformation of a solid into a liquid, melting, are, as yet, imperfectly understood, although various models have been proposed to account for this important (first order) change of state. Whereas some aspects of the premelting behaviour of solids, at temperatures immediately below the T_m, have been investigated in detail, much less is known about the dispositions and interactions between components within the liquid that is formed at temperatures at and

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immediately above the T_m. In 1978, Ubbelohde [1] emphasized that our knowledge of the molten state was incomplete, including the relationships between thermodynamic properties and structures. It is probably realistic to state that the subject has not advanced remarkably in the subsequent quarter of a century. The principal purpose of the present article is to consider aspects of the available data, specifically for the alkali halides, to formulate a useful model for their fusion. The representation proposed here is intended to characterize the changes of ordered spatial dispositions that occur between components on melting. The pattern of behaviour identified may be of more general value in extending our understanding of fusion phenomena.

Alkali halides have been widely selected as suitable model systems for comparative experimental and theoretical investigations of melting, e.g. [2]. Recognized advantageous properties of this crystal set include their simple cubic lattice structures, resulting from almost complete dominance of solid cohesion through strong bonding by spatially undirected electrostatic interactions. All twenty salts show closely comparable structures. Large and relatively perfect crystals can be prepared for experimental investigation. Modeling of behaviour is more easily undertaken for these simple salts than for most other comparable groups of solids and results are widely accepted as being generally reliable. The present paper extends and develops the melt model discussed for metals [3].

Here the extension of this model [3], to account for properties of the alkali halides, analyses the extensive physical data available in the literature. It was occasionally necessary to select the information to be used from between alternative published values that were not in precise agreement, such as ionic radii [4], and the variations of ionic radii with coordination number [5]. Consequently, the comparisons made below have been based exclusively on the published quantitative measurement sets that were identified as being the most reliable and consistent available. Sources are cited to provide authoritative foundations for these conclusions. The author has gained the impression from the literature that it has been customary to regard the alkali halides as a single group of structurally identical 6:6 coordinated cubic crystals, with the two exceptions of CsBr and CsI which remain 8:8 coordinated to the T_m [6]. In the present analysis, one possibility explored is that there may be significantly different (and interesting), sub-groups that can be distinguished within this set of apparently closely comparable salts.

The principal conclusion from the present comparative analyses of the physical changes that accompany melting is that modifications of the local (interion) structural dispositions, between the two condensed states of matter, crystal and melt, may be less profound than is often apparently (and implicitly) accepted. Nevertheless, the long-range order (and rigidity) of the solid-state is lost on liquefaction. The liquid is regarded, in the treatment below, as a transitional state of matter that, in the range immediately above its T_m, retains structural features of the solid, from which it has been transformed without sensible temperature change. Fusion is invariably described as occurring at a melting point and no range of temperature across which the phase change proceeds is ever mentioned: this will be discussed in Part 3. During any subsequent temperature rise, across which the liquid is stable, systematic structural modifications (increasing disorder) anticipate subsequent conversion of the components of the liquid to their (much) greater mobility in the gaseous-state. For example, the physical properties of liquid water are largely determined by extensive retention of the intermolecuar hydrogen bonding that dominates the structure of ice, but this becomes much less significant after volatilization.

Theories of melting

A comprehensive review of this important subject is not attempted in this research paper. The book by Ubbelohde [1] provides an authoritative survey to the mid-1970s and is particularly valuable in being concerned with ‘the molten state of matter’. The melting of alkali halides was specifically considered in 1990 by Shanker and Kumar [2], who, in the second sentence of their valuable review, state with reference to melting generally: ‘its physical mechanism is not properly understood’. They distinguish two alternative approaches in the relevant literature. The first is based on the requirement that, at the T_m, there is equality of free energy for both solid and liquid-states, which must include the melt structure, sometimes described as quasicrystalline. The second is concerned with the characteristic changes in the solid as the T_m is approached. In comparing and contrasting the principal theories that have been proposed [2], this review cites many literature sources, giving access to the extensive publications available. There is, however, relatively little information about ionic structures in the liquid phase.

The temperature at which a solid melt is, according to Van Uitert [7] ‘an important but not too well understood property of materials’. He [7, 8] identifies melting point with crystal cohesion, a measure of bond strength, and, for several sets of mainly ionic compounds (including the alkali halides), discusses trends of magnitudes of T_m with lattice spacings, ionization potentials and electron affinities of the components in the crystals concerned. Bosi [9] relates T_m values for alkali halides (and alkaline earth oxides) to the electrostatic attractions between the constituent ions and the ratio of heat of fusion to lattice energy. Again for the alkali halides, Rosseinsky and Stead [10] find an empirical relationship giving acceptable constancy of the product T_m (lattice spacing)$^{2/3}$.

An alternative approach to the theoretical representation of melting proceeds from the view that imperfections, similar to those familiar in solid-state chemistry, may be present in liquids at relatively higher concentrations. Their prolific generation has been proposed as an explanation for fusion. Pathak and Vasavada [11] show that coefficients of expansion of several alkali halides increase linearly with temperature to about $0.7T_m$, and above this temperature the relative increase in expansion rate may be identified with a rise in concentrations of thermally generated Schottky defects. Vaid *et al.* [12] developed a disorder model in which melting is treated as a 'quasi-discontinuous increase in the concentration of thermodynamic «defects»', taken as a 'variable depending on the structure of the solid and of the melt, simply based on the concept of packing fraction'. Liquid structures and melting temperatures were discussed for the alkali halides with reference to the liquid Madelung energy and the Schottky defect energy by March and Tosi [13]. For the alkali halides, Ksiazek and Gorecki [14, 15] present a vacancy model in which the crystal melts when the concentration of Schottky defects reaches the critical concentration of 0.0017. Melting is then accompanied by a large, discontinuous increment in Schottky defect concentration to approximately $\Delta c \approx 0.15$.

Earlier, the alternative approach by Kuhlmann-Wilsdorf [16] identified fusion with the unrestricted proliferation of dislocations (line defects) in the crystal structure, when the free energy of glide dislocation cores becomes negative. McGreevy and Pusztai [17] have used neutron diffraction to measure neighbour distributions within molten halides. From comparative studies for alkali chlorides, it is concluded that unlike ion distributions in LiCl, NaCl and CsCl show coordinations that are close to 5, 5 and 6, respectively.

A literature search revealed no recent general review of the physical basis of melting and no novel and comprehensive theory of fusion was identified in current publications. While much progress has been made, no quantitative explanation of the mechanisms of melting or identification of the factors that control the transformation of solid crystal to liquid melt was found. It was, therefore, considered to be of interest to examine some of the more chemical aspects of the phenomenon and the results obtained are reported here, based on published data available for the alkali halides. In this series of articles, four specific aspects of the melting of alkali halides are considered individually and their interrelationships explored. (*i*) Fusion enthalpies are compared with differences of lattice energies calculated for the alternative structures having 4:4, 6:6 or 8:8 ionic coordinations; (*ii*) The densities of solid and liquid-states in the vicinity of the T_m are compared to estimate the relative proportions of the possible alternative, locally ordered, coordination structures that are capable of accounting for melt densities; (*iii*) In Part 2, the melting point-temperature phase diagrams for binary mixtures of alkali halides, previously comprehensively and critically reviewed [18], are comparatively examined in the context of the conclusions obtained from (*i*) and (*ii*) above; (*iv*) In Part 3, aspects of the thermodynamics and temperature constancy of melting are to be discussed in the wider perspective of other chemical and physical properties that change with temperature.

A theoretical model capable of representing melting would have considerable potential value in providing insights into the changes that occur at T_m and the properties of melts. Relationships between structures and physical properties of materials have been discussed [19], enthalpies of melt mixing vary with compositions [20] and values of T_m may depend of crystallinity [21]. In glass-forming melt mixtures, crystallization may be complex and result in formation of different products [22], bond strengths may be related to viscosity [23] and rates of crystallization have been studied [24]. Crystallization of compounds composed of large molecules, such as polymers, sometimes involves complex rearrangements [25], in contrast with the rapid, and readily reversible, adoption of simple crystal structures, characteristic of simple ionic salts, including the alkali halides.

Methods and objectives: a model for melting

The purpose of this review/analysis is to characterize, as far as can be ascertained from the physical evidence available, properties and permissible structures of the alkali halide melts. From quantitative examination of published data for the changes of energy and density that occur during the fusion of each salt, inferences are made about the likely forms and extents of the spatial reorganizations of the lattice components that accompany loss of crystal long-range order and rigidity. This approach has not, apparently, been previously applied quantitatively and in detail. The loss of extended order above the T_m means that X-ray diffraction methods, so successful in establishing structures of solids, have little value for determinations of properties and structures of melts. This dearth of information, about the relative dispositions of ions in the fused salt at the T_m, is widely accepted as an important constraint on our understanding of the controls and mechanisms of the solid/liquid transition. Nevertheless, discussions sometimes imply or refer to melts as quasicrystalline [1, 2, 12–15] and apply, in consideration of their properties, concepts and models that were originally developed for use in describing crystalline solids. The present comparative examinations identify a specific form of this quasi-crystalline model that represents the types and extents of lattice modifications that occur during alkali halide fusions. This is regarded as a potentially valuable approach because, during the melting of each salt, energy and density changes are relatively small, which is evidence that elements of the structural integrity of the crystal are retained after liquefaction.

The quantitative and comparative analysis of the relevant literature data, presented below, demonstrates that density and enthalpy changes on melting of the alkali halides are always small. Consequently, there can be only minor changes in structural order on fusion. This results in either a slight decrease in packing order of a majority of the ions or more profound structural rearrangements of a small proportion of those ions. The model proposed below incorporates both possibilities. The essential premiss is that the physical changes at T_m demonstrate that there must be extensive retention of packing order within the relatively dense and stable assemblages of ions of constant size and charge. The strong tendency for ions of opposite charges to adopt regular three dimensional arrangements can be expected to persist in the liquid. The physical changes at T_m are simply too small to accommodate significant disorder.

The set/liq melting model: a proposed representation of the liquid at T_m

This melt model portrays the liquid immediately above T_m as a compact assemblage of contiguous zones, within each of which the ions are closely packed in one or other of the possible alternative, relatively stable, regular lattice structures. The thin contact interfaces between neighbouring zones of regular arrays are less ordered, forming transition material composed of mobile ions of (mainly) lower coordinations. Continuous, and probably rapid movements of ions in both directions, transfers between adjoining regular zones, maintains the dynamic character of the fluid assemblage and confers its liquid character. The 'single extended tessellation' of the regular crystal is lost on fusion to be replaced by the 'lattice interconversion quadrille' ('quadrille' – a structured form of dance): this representation of melting will be referred to here as the set/liq model.

The changes of density and of enthalpy on alkali halide fusion are relatively small, and are discussed quantitatively below. Because the strong, but unoriented, electrostatic attractive and repulsive interactions between the ions are unlikely to be changed at the T_m, it is expected that local ordered relative dispositions of ions will be maintained into the melt. The forces controlling such relative dispositions of neighbouring ions remain the same as those applicable in crystals, which for each solid forms only the single (most stable) lattice structure. From this we conclude that the spacings of adjacent ions in the liquid (regarded as 'touching' spheres) must be comparable, even locally identical, with the conventional dimensions for ionic packing in crystals. The electrostatic interactions controlling spherical ion packing in both crystal and melt phases are expected to be subject to the same controls and constraints, both above and below T_m. A principal conclusion, derived from this comparative and quantitative analysis, is that the energy necessary to convert solid into liquid is insufficient to modify substantially the (electrostatic) ionic interactions that stabilize the crystal structure of each alkali halide.

Theoretical calculations of crystal energies indicate that, for most of the alkali halides, there are alternative packing arrangements, in addition to those characteristic of the known solids, which have only slightly lower stabilities. Accordingly, it is suggested here that, at the T_m and above, the restriction that a single structure only can be present (as in the crystal) is relaxed and local zones having alternative and stable regular structures can coexist, participating in dynamic equilibria. This transformation requires energy, the fusion enthalpy, ΔH_F, to maintain the (slightly) less stable packing forms together with the necessarily disordered material that constitutes the contact interfaces between contiguous, regular zones (each is small, with crystal-like order). The long-range crystal order is lost and the enhanced mobility of at least a proportion of the constituents accounts for the fluidity of the liquid phase. The ΔH_F, that maintains this dynamic situation, represents only a small proportion (usually less than 5%, see below) of the total crystal lattice potential energy. Nevertheless, at the T_m some lattice components achieve enhanced mobility and ΔH_F stabilizes the overall changes that occur on forming the dynamic melt.

On this set/liq model, two properties distinguish the melt from the solid. The small zones of regular structure, closely packed ions, are composed (for the alkali halides) of domains having alternative and stable regular ionic dispositions based on 4:4, 6:6 and/or 8:8 coordinations. It is shown below that, for some alkali halides, alternative ionic dispositions with 4:4 and 8:8 coordinations have estimated stabilities that are often close to values for the (usual crystal-stable) 6:6 form. It follows that, when sufficient energy is available to destabilize the (preferred) rigid lattice structure of the solid, the fusion process, other energetically acceptable alternatives may be adopted. Second, there is continual and rapid transfer and/or structural interconversion of ions between the coexisting and contiguous, different possible structures. Such a liquid can be termed an autoeutectic. When, during cooling, the available energy becomes insufficient to sustain the dynamic equilibrium between the different forms, the liquid solidifies with the loss of the 'liquefaction energy excess', the enthalpy of fusion, ΔH_F, and the crystal is formed through adoption of the single, the most stable, structural arrangement.

The proposed set/liq representation distinguishes two structurally distinct regions that together form contiguous contacts in the compact assemblage that constitutes the liquid.

- Regliq: this term specifies each individual small zone of the liquid within which the regular dispositions of ions attain a local order that approaches the structural perfection of a crystal. (Such zones are analogous to 'grains', the more perfect domains, in crystals.) For the alkali halide melts, it is suggested that, in general, two or more types of regliq regions of approximately comparable stabilities may coexist. The size of each individual zone must be small, below the dimensions required to give effective reinforcement of X-rays by diffraction. This applies when particle diameters are below 'roughly 20–100 Å' [26]. In the dynamic model proposed, the equilibrium resulting from transfer of material between contiguous zones will result in the continual (?nucleation→) growth and shrinkage of each and every individual regliq zone ('grain'), giving these a range of sizes.
- Irregliq: contacts between regliq zones are regarded as analogous to the 'grain boundaries' in crystals [27], forming an interconnected web of less-ordered irregliq material that extends throughout the total volume of the liquid. Such interfaces, attaching neighbouring regliq zones ('grains'), are composed of ions of lower, incomplete, anomalous, and/or locally distorted coordinations interposed between the alternative (regliq) zones of regular structures. The thicknesses of such layers of interfacial connective material are expected to be limited to a very small number of ions (one or two 'molecular' layers). Ions within this irregliq material, 'in transition' between the more stable adjoining regions, are relatively easily moved. The lower coordinations and irregular dispositions of the more mobile ions participating in dynamic rearrangements confer overall fluidity to the liquid phase. The continual and facile movements of material across the (thin) interface between the regular zones confer the fluid properties on the liquid: strain cannot be maintained within these dynamic assemblages of interfacial ions, which undergo constant relative repositioning. (Material in 'grain boundaries' of a solid, is similarly regarded [27] as strained and consequently relatively mobile and reactive.)

Ions within zones of both types experience an overall resultant electrostatic force, giving each local assemblage the cohesion that tends to minimize the total volume, thereby maximizing densities, which are less (usually by 10–30%) than that of the crystal. The enthalpy of melting contributes to the ability of the relatively less-stable regular structures to participate in the equilibrium. Energy derived from the ΔH_F also sustains the more disordered and mobile ions within the (dynamic) irregliq zones.

In summary: the subsequent analyses consider the applications to alkali halides of the representation of the set/liq melts as highly dynamic, compact assemblages of contiguous and interconverting small zones (regliq). Each regliq zone approximates closely to one or other of the (energetically favoured) ordered packing arrangements of the alternative possible crystal-type forms of the salt. The less ordered connective material (irregliq), represented by the transitional and mobile ions that participate in the interconversions between the contiguous stable regliq zones, accounts for melt fluidity. Continuous and rapid interconversions of these structures, by maintained dynamic transfer of material between zones throughout the melt, means that the thin irregliq interfaces may move within the liquid. The overall disposition of ions is thus envisaged as a dynamic analogue of a solid eutectic (though requiring retention of greater total energy). Melts represent more ordered and less energy-rich systems than freely moving gaseous molecules.

The comparative analyses of literature data presented below are concerned specifically with the changes in enthalpy, ΔH_F, and in density on melting at the T_m. Calculation of crystal lattice enthalpies by the Madelung method [28] requires knowledge of internuclear separation distances and densities were determined using the unit cell edges at the temperature of interest (the T_m). The necessary data for every alkali halide were not found in the literature but values obtained from [11, 29, 30] showed that unit cell edges expanded by between 2.5 to 4.0% on heating from ambient temperature to the T_m. Where possible, published values were used but, for the few magnitudes that were unavailable, estimates were made from the known T_m and listed thermal expansion values for salts with common ions: the errors introduced by this correction are probably very small.

Lattice energies

For the spherical ions of the alkali halides, the dominant controls of structures and stabilities of the ionic crystals are the (non-directional) coulombic attractions and repulsions. Cations and anions may approach each other until the electrostatic attractive forces are balanced by repulsion through overlap of outer electron clouds. For spherical ions, the regular packing pattern is determined (to some extent) by the relative sizes of the constituent ions. Background general theory has been given by Wells [31], including the crystallographic properties of the alkali halides, for which the bonding forces are predominantly electrostatic. However, the structures predicted through the use of geometric packing principles based on the ionic radius ratios are not fulfilled exactly.

Lattice energy calculations

Total lattice potential energies, U_{POT}, can be calculated for suitable crystalline ionic solids, from energy changes on their formation from the elements in their standard states. Values for many representative salts are listed in [32]. Table 1 lists the calculated (theoretical) crystal lattice energies, using the Madelung formulae [28] for 4:4, 6:6 and 8:8 coordinations (U_4, U_6 and U_8) of the alkali halides, together with enthalpies of fusion, ΔH_F, [14] and aggregate heat capacities to T_m, ΣC_{ps}.

The crystal lattice energy, U, can be calculated from Eq. (1) [28]: the dominant energy terms are (+Coulombic attraction–Born repulsion):

$$U=NMe^2r^{-1}(1-n^{-1}) \qquad (1)$$

where each ion bears single unit charge, N is the Avogadro number, M is the Madelung constant (taking account of the attractive and repulsive components of the electrostatic interactions for each specific crystal structure), e is the electronic charge, r is the shortest (centre) separation distance between ions of opposite charge and n is the Born exponent (listed in [28]) representing the repulsion term.

Two other smaller terms contribute to the total crystal energy: the van der Waals, or London, attractions and the zero point energy [31]. For NaCl, these represent only about $+0.017U_{POT}$ and $-0.010U_{POT}$, respectively, and act in opposite directions, thereby partially cancelling. In the present analysis, particularly concerned with stability comparisons for alternative coordination dispositions involving the same ion pairs, these differences will be even smaller and their contributions have been omitted from the present discussions. This is, however, a minor source of possible error and should be remembered as an inaccuracy, perhaps representing about 5 kJ mol^{-1} (or less) in U values listed in Table 1.

The crystal lattice energies listed in Table 1 were calculated using the appropriate Madelung formulae (Eq. (1), [28]) for structures based on 4:4 (zinc blende, face centred cubic), 6:6 (sodium chloride, rock salt) and 8:8 (caesium chloride, body centred cubic) coordination arrangements, U_4, U_6 and U_8, respectively. While alternative structures are not found for most of the crystalline alkali halides, except the 8:8 forms of CsCl, CsBr and CsI [6, 31], many of the stabilities calculated theoretically are similar in magnitude to those of the preferred 6:6 coordination characteristic of the

Table 1 Crystalline alkali halides: values of total lattice potential energies, U_{POT}, from [32], calculated (theoretical) crystal lattice energies from Madelung formulae [28] for 4:4, 6:6 and 8:8 (U_4, U_6 and U_8) coordination, enthalpy of fusion [14], aggregate heat capacity, ΣC_{ps} ('Aggregate specific heat, integrated to the T_m (ΣC_{ps})') and melting point

Salt	U_{POT} from [28]/ kJ mol^{-1}	Lattice energies calculated from Eq. (1) 4:4 U_4/ kJ mol^{-1}	6:6 U_6/ kJ mol^{-1}	8:8 U_8/ kJ mol^{-1}	ΔH_F [14]/ kJ mol^{-1}	Aggregate heat capacity to T_m, ΣC_{ps}/kJ mol^{-1}	T_m [18]/K
LiF	1030	950.1	**930.6**	853.8*	27.08	47.48	1121
NaF	910	808.3	**851.4**	804.1	33.62	60.97	1269
KF	808	712.4	**757.3**	729.0	28.25	55.98	1130
RbF	774	684.2	**729.6**	713.6	25.74	57.98	1066
CsF	744	651.3	**694.8**	686.4	21.72	51.66	976
LiCl	834	789.0	**786.1**	669.5*	19.92	41.38	883
NaCl	769	683.8	**722.0**	683.5*	28.00	54.51	1074
KCl	701	617.6	**656.7**	636.4	26.54	54.13	1044
RbCl	680	593.6	**633.3**	621.9	23.73	50.30	993
CsCl	657	571.8	**609.8**	**603.0**	20.26	49.40	918
LiBr	788	747.3	**747.4**	603.9*	17.66	39.02	823
NaBr	732	655.8	**692.8**	614.9*	26.12	52.30	1020
KBr	671	590.2	**628.3**	610.1	25.53	54.04	1007
RbBr	651	577.2	**609.6**	599.4	23.31	49.74	967
CsBr	632	553.2	590.4	**584.1**	23.62	46.41	908
LiI	730	695.3	**696.0**	545.2*	14.65	36.42	742
NaI	682	616.6	**648.6**	552.8*	23.61	48.32	933
KI	632	557.2	**592.9**	564.5*	24.03	51.17	954
RbI	617	539.9	**575.6**	567.2*	22.06	47.79	920
CsI	600	523.3	558.3	**553.1**	23.61	48.02	913

Bold entries identify known crystal structures; lattice energy values U_4, U_6 and U_8 were calculated for lattice spacings at the T_m; *crystal unit cell dimension defined by the diameter of the larger anion.

known solids. It is suggested here that these alternative structures exist together in the liquid, due to accommodation of the fusion enthalpy above the T_m.

All the values of U_4, U_6 and U_8 listed in Table 1 were calculated using the coordination energy formulae and M values given by Lide [28], with the appropriate ionic radii [5]. Some r values for different coordination forms of the same salt were equal [5], the differences in lattice energy for alternative packing arrangements then result from the appropriate Madelung factor. All internuclear separations, r in Eq. (1), were those applicable at T_m using the listed thermal expansions for each salt [11, 29, 30] or (for those not available) the interpolated value, obtained as described above. (Melting points for the structures of the unknown crystals presumably coincide with those of the known forms, where T_m may then be identified as the minimum temperature for facile interconversions in the melt. The transition 8:8↔6:6 for CsCl at 742 K [6] is below the T_m, 918 K, at which facile interconversion and equilibration may then become possible. The values identified by * in Table 1 refer to 8:8 coordination in which the ionic structure is defined by the anion–anion separation, because the cation incorporated within the unit cell cube is too small to maintain contact with all eight anion neighbours: U_8 values are diminished accordingly).

Enthalpy of fusion (latent heat of melting)

The ΔH_F values for alkali halide melting are small (14–34 kJ mol^{-1}) compared with total lattice potential energies, U_{POT}, (600–1030 kJ mol^{-1}, Table 1 [26]), the crystal lattice energies (523–950 kJ mol^{-1}) and the enthalpies of vaporization [33], for these crystals which melt at relatively high temperatures. The minor energy input required to achieve fusion at T_m is a principal reason for concluding that the changes of local, short-range order during fusion must be comparatively small, even though long-range order is lost. The analyses below consider, together with the density changes, the significances of the enthalpy differences, calculated from Eq. (1), for the alternative (theoretical) structures based on 4:4, 6:6 and 8:8 coordinations, calculated from Eq. (1). Many of these ionic arrangements do not appear as crystalline solids, some are highly improbable on stereochemical grounds, where cations are smaller than the octahedral cavity within the anionic assemblage in 8:8 structures. These are marked (*) in Table 1 and, as expected, give relatively low U_8 values. A problem in discussions of the significance of energy absorption during melting (ΔH_F) concerns estimations of the relative proportions contributing to each of the distinct endothermic processes that occur, which (presumably) include the following. The absolute and relative amounts of energy involved in each of these processes are not known and the proportions may vary between the different salts.

(*i*) To enable the formation, on melting, of appropriate proportions of the alternative regular ionic structures. This, as described above, is the generation of those regliq zones wherein the regular coordination structures of ions are different from, and less stable than, those of the precursor solid. (For the alkali halides, the proportions of such structures that may be present above T_m are estimated below from the data in Table 1.); (*ii*) to provide the energy required to maintain the irregliq zones. Within these there are enhanced thermal movements of the components in the locally less regular material, relaxed from the rigid lattice by melting. Mobility of (at least a proportion of) the constituents of the liquid is an essential pre-requisite for fluidity. On the model proposed, this may be achieved by facile changes of coordination states of the ions within the irregliq zones, also enabling more extended diffusive migrations of components throughout the liquid. Two interrelated features of this energy may be distinguished. Structural: the necessity to diminish average coordination numbers of ions within the connective, but less ordered, interfaces. Mobility: energy associated with the movement, migration and transfer of ions within the disordered irregliq zone. (As with the 'grain boundaries' of solids, the irregliq contact areas are expected to possess relatively greater reactivity, lower stability, and participate in the dynamic transfer of material between the relatively more stable, neighbouring regliq zones.); (*iii*) to replace the extended lattice stabilization energy of the crystal that is diminished by the loss of long-range order.

The comparative analysis given in 'Discussion' below considers the energy absorbed by the solid during melting, together with the concurrent density changes, to estimate the types and the proportions of different local coordination (regliq) structures that may be present in the liquid, (*i*) above. This is interpreted to identify the structural and other properties of the melt formed and to investigate whether the available experimental evidence can be realistically portrayed by the model proposed here. The essential feature of this model is that the density changes and energy absorbed are much smaller than would be required to permit rapid, free movement and low coordination of all the ions that would constitute an extensively disordered liquid. Retention of the stabilizing features of the crystal into the melt is regarded as a necessary feature of any explanation of the (relatively small) energy and density changes that accompany fusion, particularly for these simple and highly ionic salts.

Aggregate specific heat, integrated to the T_m (ΣC_{ps})

Estimates were made of the total energy absorbed by the solid, the aggregate heat capacity, on heating from 0 K to T_m, ΣC_{ps}: values are listed in Table 1. The energy required to heat each crystal to its Debye temperature, θ_D, (up to 40% of ΣC_{ps}) was obtained by numerical integration using data from [34]. Specific heats at 400, 600, 800 and 1000 K are listed in [33], magnitudes showed approximately linear increases with temperature, enabling the total energy uptake to the T_m to be calculated. These data were used, for this summation, in preference to the somewhat higher values listed for the vicinity of the melting point [15] and the enthalpy associated with Schottky defect formation [15]. Magnitudes of ΣC_{ps} were approximately constant, the energies absorbed to the T_m (including the contribution below θ_D) by all the Na, K, Rb and Cs halides were 52.05±3.88 kJ mol^{-1}: values are listed in the seventh column of Table 1. Values for the lithium salts were relatively lower. No reasons were apparent for the relatively high NaF and RbF values and the low CsBr value: these represent more than half the±error limits).

This pattern of behaviour offers a simple, and superficially attractive, explanation for fusion: alkali halides melt when the aggregate vibrational energy reaches approximately 52 kJ mol^{-1}. This model is, however, difficult to reconcile with other, significantly different, properties of these salts and is discussed further in Part 3. It is not obvious why long range order should be lost at a constant ΣC_{ps} value (Table 1) for a set of crystal structures which have stability energies that vary by a factor of almost two.

Density comparisons

Densities of the crystalline and the liquid [35] alkali halides at T_m are listed in Table 2, together with theoretical values calculated, from atomic masses and unit cell volumes, for the possible alternative lattice structures having 4:4, 6:6 and 8:8 coordinations. Comparisons were undertaken to determine whether liquid mixtures composed of these structures are capable of accounting for the observed significant diminutions of densities on fusion of the alkali halides [1, 36]. This possibility is reasonable because the density of each melt, immediately above the T_m, is within the range calculated for mixtures of ionic structures having 4:4, 6:6 and 8:8 coordinations, consistent with close packing and maintaining contacts between neighbouring ions. It is assumed that spatial ordering within the melt is controlled predominantly by the strong attractive and repulsive electrostatic interactions between the constituent ions, of the same type that determine the stable lattice structures of the crystalline solids. The distinctive characteristic of the melt (the set/liq model formulated here) is that the energy available above the T_m (i.e., ΔH_F) is sufficient to maintain the continual reorganizational movements of the ions between the different alternative, but locally regular and relatively stable, packing arrangements. There can be no extensive structural disordering at T_m.

Density of solids at ambient temperature

To confirm consistency of the data, comparisons were made between the density values of crystalline alkali halides listed by Lide [37] and those calculated from unit cell edges given by Wyckoff [38]. There was close agreement (less than 1% difference) for 12 of the salts with the NaCl structure and a further 4 were within ±2%. Densities of the three 8:8 coordinated salts, CsCl, CsBr and CsI, agreed within similar limits. Exceptionally, the value listed [37] for RbF, 3.2, differed significantly from that calculated, 3.868, and also from that (3.557) from an earlier edition (62nd Ed., 1981-2) of [37]. Densities similarly calculated from unit cell edges based on ionic radii (appropriate to coordination number) [5] showed slightly greater variations (±4%) than those derived from data in [38].

Density of solids at melting point

The density of each solid alkali halide at its T_m was determined from two complementary sets of published data, and values are listed in Table 2.

The density of each solid, ρ_S, was calculated from atomic masses and unit cell edge values [38], individually corrected (by +2.5 to 4.0%) for thermal expansion [11, 29, 30] between ambient temperature and the T_m. Estimated expansion values were used for the few salts for which data were not available.

Ubbelohde [1] Table 8.1. of [1], see also [36], has listed thermodynamic melting parameters for 14 alkali halides, including (%) volume change of the solid on melting, $[100(V_L-V_S)/V_S]$. Similar values, though not all are identical, together with two additions, are given by Ksiazek and Gorecki [14]. The density of each solid, ρ_S at the salt T_m, was calculated from the liquid density, ρ_L, also at the T_m [35], and the listed [1, 14, 36] volume change on melting.

All density values, ρ_S, determined from these alternative data, agreed within ±2%, for the salts listed in [1, 14, 36], with the single exception of KCl (+5.3%) for which the magnitude is (apparently and exceptionally) also out of sequence in Table 8.1. of [1]. Densities, ρ_S, estimated by interpolation for salts omitted from [1, 14, 36] agreed, within similar error limits (±2.5%), with values obtained as described in the previous paragraph. The estimates for CsCl, CsBr and CsI

Table 2 Densities of solid and of liquid alkali halides at each T_m and calculated (theoretical) crystal densities at the same temperature for alternative regular structures based on 4:4, 6:6 and 8:8 coordinations

Salt	Density liquid [35], ρ_L/g cm^{-3}	Density solid [1, 36], ρ_S/g cm^{-3}	Calculated crystal density, 4:4 ρ_4/g cm^{-3}	Calculated crystal density, 6:6 ρ_6/g cm^{-3}	Calculated crystal density, 8:8 ρ_8/g cm^{-3}
LiF	1.81	2.342	1.758	2.372	2.035*
NaF	1.948	2.482	1.612	2.516	2.542
KF	1.910	2.239	1.436	2.265	2.466
RbF	2.87	{3.386}	2.227	3.438	4.074
CsF	3.649	{4.087}	2.682	4.137	5.024
LiCl	1.502	1.896	1.513	1.913	1.358*
NaCl	1.556	1.945	1.288	1.909	1.818*
KCl	1.527	1.791	1.144	1.787	2.016
RbCl	2.248	2.569	1.616	2.579	2.983
CsCl	2.79	3.083	1.972	3.072	3.660
LiBr	2.528	3.142	2.548	3.125	2.160*
NaBr	2.342	2.867	1.932	2.868	2.559*
KBr	2.127	2.480	1.568	2.481	2.765
RbBr	2.715	3.083	1.936	3.121	3.592
CsBr	3.133	{3.415}	2.195	3.380	4.154
LiI	3.109	(3.737)	2.996	3.658	2.353*
NaI	2.742	3.252	2.214	3.266	2.636*
KI	2.448	2.837	1.775	2.818	2.919*
RbI	2.904	(3.261)	2.036	3.263	3.735*
CsI	3.197	{3.453}	2.212	3.406	4.193

All density values are at T_m; *unit cell edge defined by (large) anion diameter ($2r$); explanation of the calculation methods and discussion of assumptions are given in the text, see also: 'Density comparisons'

were based on calculations assuming 6:6 coordination (which does not occur; see also [31]). These very satisfactory comparisons confirm the reliability of the density values, ρ_S, for all 20 solid alkali halides, assuming 6:6 coordination [38] at the T_m. Values are listed in Column 3 of Table 2, where all density values have been calculated to refer to the T_m.

All density values have been calculated to refer to the T_m.

Liquid densities, ρ_L, were obtained from [35] and the solid densities listed, ρ_S, were the mean of two values calculated and described above. Two additional entries were from [14] (bracketed) and four were interpolated {magnitudes}.

Densities calculated for 6:6 coordination, ρ_6, (fcc, NaCl structure)

Atomic masses were used with unit cell edge values listed by Wyckoff [38], corrected for thermal expansion [11, 29, 30], representing density diminutions of between 7–12%. Agreements of ρ_S and ρ_6 values in Table 2 are good.

Densities calculated for 4:4 coordination, ρ_4, (zinc blende, tetrahedral structure)

Unit cell edges were estimated from ionic diameters listed for 4:4 coordination [5], these may be slightly less reliable than the 6:6 values which were based [38] on specific measurements for each crystal. T_m and linear thermal expansion values were assumed to be equal to those for 6:6 coordination (apparently the most reasonable assumption).

Densities calculated for 8:8 coordination, ρ_8, (bcc, CsCl structure)

The same principles were again applied. Additionally, it was necessary to define the unit cell dimension by the relatively large anionic radius where the cation was too small to accommodate the high coordination (8) contacts in the octahedral cavity. This applied to the four lithium halides, NaCl, NaBr, NaI, KI and RbI: these values are marked * in Table 2.

Data accuracy and error

The absolute accuracies of all the data used in these comparisons are not known: the tabulated values do not include uncertainty estimates. A problem is that the precisions of individual entries in any listing may be appreciably different. A specific source of error is the purity of the samples used for the measurements, see notes to Table A1 of [18]. Other unknown features include the influences of criteria used to determine the consistent listing of values of ionic radii, their variation with coordination number and their effective increases with temperature (if any). All values used here have been taken from sources that appeared to be reliable and are specified (though these judgements are ultimately subjective).

From the quantitative data in Table 2, the following generalizations and deductions were made for the alkali halides in the vicinity of each T_m.

Densities of the solid alkali halides

These are entirely in accordance with expectation for 6:6 coordination, except for CsBr and CsI which, at the T_m, are 8:8 coordinated, presumed [31] to be due to a contribution from polarization energy.

Halide melts containing K^+, Rb^+ or Cs^+

Densities of these twelve melts fall comfortably between magnitudes for 6:6 coordination, stable for all the crystalline solids (except CsBr and CsI) and (theoretical) expectation for 4:4 coordination. Densities (estimated) for 8:8 coordinations are all greater than the 6:6 values, suggesting the presence of minor proportions of this structure in these melts.

Halide melts containing Na^+

Calculated densities for the 6:6 and the 8:8 coordinated structures in NaF are close and the theoretical 8:8 densities relatively decrease in comparison with the 6:6 values in the sequence NaCl, NaBr, NaI. It is, however, believed that 6:6 coordination is probably the preferred disposition because 8:8 coordination of the larger anions around the relatively small Na^+ cation is expected to be inhibited by stereochemical considerations.

Halide melts containing Li^+

Densities of LiCl and LiBr melts are very close to expectation for 4:4 coordination, and the values for LiF and LiI melts are consistent with the presence of only small proportions of 6:6 structures. It is even less probable (than for Na) that this small cation participates in stable 8:8 coordination.

Comment

Magnitudes of the density diminutions (Table 2), that characterize the melting of alkali halides [1, 14, 36], are entirely consistent with the proposed set/liq melt model that envisages extensive retention, as large numbers of distinct small zones, of the structure of the precursor crystal. The observed density changes, $\rho_S-\rho_L$, at T_m, are consistent with the retention of an appreciable proportion of mainly that structure which has the (geometrically) most probable alternative ionic arrangement, 4:4 or 8:8 coordination.

Discussion

The data summarized in Tables 1 and 2 confirm that the enthalpy and density changes that accompany alkali halide melting are relatively small. The evidence is that, after fusion, the interionic distances remain similar to those of the precursor solid. Because the relative dispositions of ions must remain subject to control by the same dominant electrostatic interactions, it is concluded that the structures in melts are closely similar to those in crystals. The additional energy acquired on melting, ΔH_F, is ascribed to the enhancement of mobility of (at least) a proportion of the constituent ions. Freedom of component movement is an essential fluid property. ΔH_F is also regarded as promoting the coexistence and interconversion of those regular (lattice-type) structures that are only slightly less stable than the (single) form that characterizes each crystalline solid.

In this analysis, the set/liq model is applied to the alkali halides. The arrangements of ions in each melt at T_m is represented as an assemblage of local zones, each of limited extent, and having one of the possible alternative, regular and stable, structures (4:4, 6:6 or 8:8 coordination). Estimates, given below, of the proportions of these structures in each of the melts are based on the enthalpy and density changes that occur at T_m (Tables 1 and 2). From these data, it is, however, not possible to determine, unambiguously and precisely, unique proportions of each of the alternative structures that are present in every molten salt. Various different relative amounts of the (three) constituent forms can (usually) account equally satisfactorily for the observed density changes. The proportion, or absolute amount, of ΔH_F associated with the component phase changes for each individual salt is not known, because this composite term also accommodates the energy required to form the irregliq zones ('Enthalpy of fusion (latent heat of melting)'). Nevertheless, these comparative analyses demonstrate that the physical changes on melting are entirely consistent with the set/liq model proposed. Moreover, the quantitative comparisons presented below estimate the most probable structural compositions for most of the alkali halide melts, together with estimated limits for their possible variations.

An unexpected outcome of these comparisons is that distinctive trends for melting have been recognized as sub-sets within this group of salts that hitherto appear to have been regarded (and treated) as a single, similar and comparable set. Recognition of these differences, particularly in regarding the lithium halides as a sub-set, may have value in advancing theoretical understanding of alkali halide melting (and, perhaps, of other salts).

The proposed set/liq model for melting is intended to provide a theoretical framework for the systematization of experimental observations, an essential feature of the scientific method. The value of theoretical concepts in providing a rational foundation for the correlation of observational data has been emphasized by Laidler [39] (with reference to the Arrhenius equation) and by Taplin [40] (for kinetic analyses). Without a suitable theoretical model, information remains empirical: the phenomenon of melting, at present, appears to lack a suitable representational explanation. The approach advocated here is intended to focus attention on the existence of structural similarities, together with the other physical differences, of the crystalline and liquid phases in the context of the characteristic discontinuous changes that occur at the T_m. This concept may be capable of wider application and further development. These analyses have been made because other available models apparently have not yet been generally accepted as foundations for theoretical advances.

Melting of the lithium halides

The data in Tables 1 and 2 exhibit several distinctive features that suggest lithium halide melting should be classified as a separate sub-group, exhibiting properties that are recognizably different from the behaviour of the other alkali halides. Although LiF possesses the highest total lattice potential energy [32] (120 kJ mol^{-1} greater than the next largest, NaF) its T_m is 148 K below that of NaF. The greater ease of fusion of LiCl, LiBr and LiI, compared with the other alkali halides, is apparent in their relatively lowest T_m values, the ΔH_F values (Table 1) and the heat capacities aggregated to the T_m (Table 1).

For LiCl, LiBr and LiI, the relatively low T_m values can be explained by the facile conversion of the 6:6 coordinated crystal to 4:4 coordination in the liquid. The latter is in accordance with expectation [31] for the preferred geometric ionic arrangement, based on the radius ratios (the value for LiCl, 0.420, is only just outside the 4:4 limit at 0.414). This conversion, 6:6(crystal)$\rightarrow$4:4(melt), is entirely consistent with the small energy changes estimated for this transformation, Table 1, less than 3 kJ mol^{-1} (theoretical 8:8 structures, sterically hindered and considerably less stable, are not considered further). This is also consistent with the liquid densities, which were remarkably close to expectation for 4:4 coordination (Table 2), though an appreciable proportion (up to 20%) of the 6:6 structure appears to be retained in molten LiI. Density ratios (6:6/4:4) calculated for the lithium halides at the T_m (1.22–1.35) were significantly lower that those (1.48–1.61) for all the other alkali halides.

Occupancies (efficiency of ion packing within the unit cell) in lithium halide crystals, defined as % unit cell occupied by the spherical ions, were always greater, most were significantly greater, than those for the other alkali halides. In 4:4 coordinated lithium salts, theoretical occupancies were 48–68% and for all other salts were 34–48%: corresponding ranges for 6:6 coordination were 71–84 and 53–71%, respectively.

LiF is characterized by a radius ratio (0.571) that is towards the middle of the 6:6 coordination stability range [31] and ΔH_F is greater than the values for other lithium salts. Moreover, the enthalpy change for the 6:6 to 4:4 transition appears (Table 1) to be relatively exothermic. This apparently higher stability of the 4:4 form is difficult to confirm at the T_m, however, because its magnitude depends sensitively on r in Eq. (1) which was taken here as 0.59 (ambient temperature) [5]. Small changes in the effective radius of the small Li^+ ion would result in significant variations of U_4. The higher relative thermal stability of LiF (T_m) could, therefore, derive from its tendency to retain 6:6 coordination.

For LiCl, LiBr and LiI, that proportion of the ΔH_F which can be associated with formation of less stable structures, (*i*) in 'Enthalpy of fusion (latent heat of melting)', is expected to be small. It appears, therefore, that the energy required to achieve the other changes associated with melting, (*ii*) and (*iii*) in 'Enthalpy of fusion (latent heat of melting)', are (from Table 1) approximately 15–20 kJ mol^{-1}. The indications are that lithium halide melts are mainly composed of ions in the 4:4 structure.

Melting of the Na, K, Rb and Cs halides

The liquid density cannot (usually) be used to determine unique values for the permitted relative proportions present of the three structures regarded as possible constituents in the melt. Accordingly, the tabulated data below, classified by cation for each set of halides, records representative calculated relative proportions, by mass, of the 4:4/6:6/8:8 coordinated constituents in the melt that are consistent with each liquid density at the T_m (Table 2). Except for the potassium salt ('Melting of the potassium halides', for which additional values are given) the second column for each set of tabulated data assumes the absence of the 4:4 form, the third column assumes the absence of the (most probable) 6:6 form and the final column represents mixtures containing approximately equal proportions of all three structures. Also included are the estimated {enthalpy/kJ mol^{-1}} changes (Table 1) associated with the transformation of the appropriate amounts of the 6:6 form (from the crystal) to the 4:4 and/or 8:8 structures (in the melt). In appraising the significance of these results, the {enthalpy} values are compared with ΔH_F. This enables some of the compositions, which are consistent with the density data, to be excluded from further consideration because the fusion enthalpy is insufficient to sustain these particular structural changes. However, quantitative determination of the proportions of the three anticipated regular structures present may not be possible because the specific quantity of energy involved in their formation, in the composite term, ΔH_F, is not known: some (unknown) amount is required to generate the irregliq phase.

Melting of the sodium halides

Densities of the molten sodium halides are between values calculated for 4:4 and those expected for both the 6:6 and the 8:8 forms, Table 2. The estimated stability differences for the 6:6→4:4 transitions decreased in the sequence NaF to NaI from 43 to 32 kJ mol^{-1}. Magnitudes for the 6:6→8:8 transformation were comparable in NaF and NaCl (47 and 38.5 kJ mol^{-1}). The much larger energy absorptions (78 and 96 kJ mol^{-1}) for NaBr and NaI suggest that this change cannot occur to any significant extent. Radius ratios [31] identify 8:8 as the preferred coordination in NaF but is 6:6 for the other sodium halides.

From the solid and liquid densities for the sodium halides, possible compositional proportions, by mass, of 4:4/6:6/8:8 coordinated constituents in the melt at T_m are listed together with the {enthalpy/kJ mol^{-1}} associated with these structural changes, as follows:

NaF	52/48/0 {22}	53/0/47 {43}	52/24/24 {34}
NaCl	47/53/0 {18}	41/0/59 {38}	44/27/29 {28}
NaBr	46/54/0 {17}	28/0/72 {66}	36/34/30 {37}
NaI	40/60/0 {13}	30/0/70 {77}	28/35/37 {44}

Those compositions, listed above, which contain significant proportions of the 8:8 form, require amounts of energy greater than the ΔH_F values, 23.61–33.62 kJ mol^{-1}, Table 1. It is concluded, therefore, that this structure is not present in appreciable amounts in these melts. The energies associated with the extents of the 6:6→4:4 transition (52–40%), shown in the second column above, are each about 60±6% of ΔH_F and account for the density diminutions. Melting of the sodium halides is, therefore, satisfactorily represented by the formation of approximately equimolar mixtures of the 6:6 and 4:4 forms, with slightly less of the latter in NaI.

Melting of the potassium halides

Liquid potassium halide densities were between those calculated for the 4:4 and 6:6 forms and the 8:8 values were somewhat larger. The energy required for the 6:6→8:8 changes were significantly less than for the 6:6→4:4 transition, as expected from the higher radius ratio, suggesting that 8:8 may be a preferred stable coordination form in KF and KCl [31]. The following mixtures are consistent with the liquid densities: listed are proportions of the 4:4/6:6/8:8 coordinations and {enthalpy/kJ mol^{-1}} associated with the extents of each transformation. Additional values are included for KCl to illustrate the trend of possible structure combinations that are consistent with the observed densities and the increasing energy requirements when both of the less stable forms, 4:4 and 8:8, are present.

KF	32/68/0 {14}	41/0/59 {35}	37/30/33 {26}
KCl	30/70/0 {12} 32/60/8 {14}	42/0/58 {28} 39/19/42 {24}	34/45/21 {18} 37/29/34 {21}
KBr	29/71/0 {11}	39/0/61 {26}	35/31/34 {19}
KI	26/74/0 {9}	40/0/60 {31}	28/35/37 {20}

ΔH_F values are between 24.03 and 28.25 kJ mol^{-1}, Table 1, which excludes several of the ratios mentioned above. Assuming that about half of the ΔH_F is absorbed by the structure change, it appears that the 6:6 coordination characteristic of the crystal remains a dominant constituent in the melt. In the second column above, 68 to 74% of the 6:6 form is found, with the remainder present in unknown proportions between the 4:4 and 8:8 forms: density and energetic considerations suggest that a significant proportion of the former is present in these four melts.

Melting of the rubidium halides

The pattern of calculated melt compositions, consistent with liquid densities, was comparable with that of the potassium halides, except for a slight increase in (most, but not all) proportions of the more highly coordinated forms. This agrees with expectation for the presence of the higher radius ratios which, excepting RbI, suggest a greater tendency to adopt the 8:8 structure.

RbF	36/64/0 {16}	51/0/49 {31}	40/28/32 {23}
RbCl	25/75/0 {10}	39/0/61 {22}	33/31/36 {17}
RbBr	24/76/0 {8}	38/0/62 {19}	32/32/36 {14}
RbI	20/80/0 {7}	34/0/66 {18}	29/33/38 {13}

The {enthalpies} of formation of the (4:4+6:6) mixtures are small (7–16 kJ mol^{-1}) compared with ΔH_F values (22–26 kJ mol^{-1}) which is consistent with the presence of a proportion of the higher coordinated (8:8) form in these melts.

Melting of the caesium halides

The indicated pattern of melt compositions, based on densities, was comparable with those of the K and Rb halides, while also continuing the trend towards increased proportions of the higher coordination forms with this further increase in cation size:

CsF	24/76/0 {10}	43/0/57 {24}	36/29/35 {19}
CsCl	18/82/0 {7}	36/0/64 {19}	29/32/39 {14}
CsBr	15/85/0 {6}	36/0/64 {17}	28/32/40 {13}
CsI	12/88/0 {4}	35/0/65 {16}	26/33/41 {11}

The enthalpies associated with these transitions are relatively smaller than those for the other halides, and also the ΔH_F magnitudes (20.26–23.62 kJ mol^{-1}). Values are, however, consistent with the presence of a proportion of the 8:8 structures in the melts, expected from radius ratio values for all four caesium halides and also as present in the crystalline phases.

Comment: potassium, rubidium and caesium halides

The estimated stabilities of possible regliq structures for these twelve salts include similarities that are regarded as significant. The fluorides are the most stable and the enthalpy values decrease with increase in anion size, F$^-$ to I$^-$. For the K and Rb salts, stabilities estimated for 8:8 coordinated structures are between those for the 6:6 (most stable) and 4:4 (least stable) dispositions. The relative values for caesium halides differed slightly in that apparent stabilities for the 8:8 structures were only about 6 kJ mol^{-1} less than those of the 6:6 structures. This pattern conforms approximately (but not exactly) with expectation for the geometric packing arrangement preferred from consideration of ionic ratios (r^+/r^- values from 0.414 to 0.732 are identified with the stable 6:6 packing and above 0.732 the 8:8 structure is anticipated: [31]). The indications are that lithium halide melts may be mainly composed of ions in 4:4 coordinated structures whereas the sodium halides give melts containing both 4:4 and 6:6 arrangements. Higher coordination structures, including 8:8, become increasingly probable as the cation volumes rise in the sequence potassium, rubidium and caesium. The estimated lattice energy changes on fusion are entirely consistent with these representations of ionic packing in the liquid. However, the information available is insufficient to permit the composition ratios of the alternative coordination structures present to be quantitatively characterized.

Conclusions

From a recent literature survey it was concluded that there is, as yet, no adequate, and generally acceptable, representational or theoretical model for the melting of solids. In contrast with the well-established chemistry of crystals, for which innumerable structures have been characterized in detail by X-ray crystallography, little is known about the spatial interrelationships of the components within the liquids that are formed when ionic solids melt. The above examination of the melting process is specifically concerned with the physical changes that occur during fusion of the alkali halides, which form a set of relatively simple, chemically similar and structurally comparable solids. Strong, non-directional electrostatic interactions between component ions are responsible for the coherent structures of the crystalline solids: most of the alkali halides exhibit 6:6 coordination. The changes of energy and of density that accompany the melting/solidification phase change of these salts are relatively small. It is unlikely that the physical properties of the component ions, particularly sizes and electrostatic interactions, undergo any significant modification at the melting point. Consequently, the tendency towards self-ordering within the assemblages of closely packed ions in the melt is expected to be maintained through the continued operation, above T_m, of those controlling forces that are responsible for generating the regular ionic arrangements that characterize ionic crystals. For the alkali halides, the present analysis shows that many of the estimated stabilities of the possible alternative lattice structures, involving 4:4 and 8:8 coordinations are closely comparable with those for the 6:6 arrangement that is characteristic of most of these crystalline solids. It is suggested, therefore, that the melting point represents the limit of thermodynamic stability of a single lattice type, characteristic of each pure crystal, so that, above this temperature, fusion and the fusion enthalpy remove this single-structure restriction. Thus, with the incorporation of the additional (fusion) energy, more than one regular disposition of components participates in, and contributes to, the dynamic ionic equilibria that are established in the liquid melt.

The central conclusion from this survey derives from the observation that the density changes on alkali halide melting are small [1, 36] (Table 2). The strong, non-directed electrostatic interactions between ions that ‘touch’, and others in the immediate vicinity, must be directed towards imposing order on the assemblage through the development of those stable regular arrangements that are familiar from crystal packing. If ionic sizes do not change across the T_m, a reasonable supposition, and because ΔH_F values are small (Table 1), there cannot be a great diminution of structural order on crystal liquefaction. The set/liq model for fusion (‘The set/liq melting model: a proposed representation of the liquid at T_m’) is consistent with these observations. Consequently, the phase change, melting, can be explained by the removal of the restriction, applicable to solids, that ion packing must conform to the single most stable structure. On this model, above T_m all the alternative and stable lattice ionic arrangements participate in the dynamic equilibrium that is the melt. The parameters determining solid structures have not been characterized quantitatively because the known crystalline solids do not all conform with geometric expectation [31]. Alternative regular ionic dispositions, of theoretically comparable stabilities, exist for several of the alkali halides (Table 1). Thus, it is suggested that, by including the energy promoting fusion, ΔH_F, different structures can be maintained as distinct zones in the liquid, through continual exchange of material. Because the dynamic interfaces between the crystal-type regular zones are in a state of perpetual flux, also rich in imperfections, these are incapable of withstanding stress or sustaining strain. The consequent facile movements of ions within the irregliq material are responsible for the fluid and flow properties of the melt.

The set/liq model emphasizes the dominance of structural order within the zones of regularity that characterize a high proportion of the melt. The contrast with alternative melting theories based on imperfection proliferation is, perhaps, more apparent than real and important parallels are to be found between these different representations.

Dislocation proliferation, Kuhlmann-Wilsdorf [16]: melting is associated with the proliferation of dislocations when the free energy of glide dislocation cores becomes negative. The set/liq model identifies the necessity to maintain equilibrium between ordered zones by transfer of ions across an extensive network of irregliq material in which (grain boundary type) disorder may be resolved into simpler component imperfections, including glide dislocations, that are constantly regenerating and rearranging. Moreover, the concept of a dislocation, as an imperfection within an ordered condensed phase, suggests locally enhanced disorder within a recognizably more structured material.

Schottky defect proliferation, Ksiazek and Gorecki [14, 15]: again the concept of vacancy proliferation requires reference to an ordered continuum in which the unoccupied defect sites are located. In the reg/liq model, the number of Schottky vacancies is regarded as being relatively small because the density changes are related to alternative packing efficiencies that differ from those of the crystalline solid. The concentrations of (amongst others) Schottky imperfections is expected to be small in the small sized (regliq) zones that comprise the dynamic mixture. Moreover, the density changes on melting show significant variations between the different alkali halides, about 3× between LiF and CsCl [1, 36].

A common characteristic of both of these representations appears to be the continued existence of extended order in the melts, which are presumably quasicrystalline. The distinguishing feature of the set/liq model is that two, or more, alternative structures participate in equilibria, which is consistent with the physical changes observed at the T_m.

[In support of the concept of structural ordering of melts by electrostatic interactions, the Debye–Hückel theory of ionic activities [41] may be mentioned. The departure of ionic solutes, from the ideal behaviour expected for a random disposition, is attributed to interactions of charged species over distances much greater than those in these alkali halide melts.]

Trends in estimated melt compositions

Representative relative proportions of possible alternative packing arrangements, consistent with density changes at T_m (Table 2), have been given in 'Melting of the lithium halides' to 'Melting of the caesium halides'. However, for each salt the absolute enthalpy, or the proportion of ΔH_F, that can be attributed to the structure change is not known. Consequently, the data available cannot be used to determine uniquely and precisely the relative amounts present in each liquid, of the most stable ionic dispositions, regarded here as structures having the regular 4:4, 6:6 and 8:8 coordinations. For LiCl, LiBr and LiI, the enthalpies of the 4:4↔6:6 transitions are small (2.9, 0.1 and 0.7 kJ mol^{-1}), and from the ΔH_F values it appears that about 14 kJ mol^{-1} may be required to generate the irregliq material etc. ('Enthalpy of fusion (latent heat of melting)' (*ii*) and (*iii*)). For most of the other salts, ΔH_F values are greater by 10 to 20 kJ mol^{-1} and these amounts of energy may be necessary to enable the accompanying structural transitions to take place and for which the enthalpies are relatively larger, Table 1. This range of values (10 to 20 kJ mol^{-1}) is comparable and consistent with the enthalpy changes calculated for the formation of the 4:4/6:6 (assuming that no 8:8 component is present) mixtures above (first column of tabulated values in 'Melting of the sodium halides' to 'Melting of the caesium halides'). These results are presented in graphical form in Fig. 1, which is simplified by using only the estimated proportions of the lower coordination components, 4:4 and 6:6, participating and any amounts of component 8:8 material present have been disregarded. The 8:8 forms of the K, Rb and Cs salts have the highest densities, Table 2, so that their presence must be associated with appropriately higher proportions of the 4:4 structure.

The significant feature of Fig. 1 is that the estimated melt compositions, the proportion of the 6:6 component present, varies in a systematic pattern with changes of both cation and anion. It may be inferred that the proportions of the more highly coordinated structures increase with sizes of the (usually relatively smaller) cations. From Fig. 1, it appears that cations exert the greater influence on melt structure and properties: the proportion of the more highly coordinated structure (crystal stable form) increases with cation size. The smallest ions (Li^+ and Na^+) apparently exerted the greatest influences: this pattern of behaviour is further discussed in Part 2 [42].

Another conclusion is that, while there are undoubted benefits in considering the melting of alkali halides as a single group, it may also be useful to make distinctions within this set of salts. The above results, for example, show that the lithium salts appear as a sub-group, exhibiting characteristic trends, and other

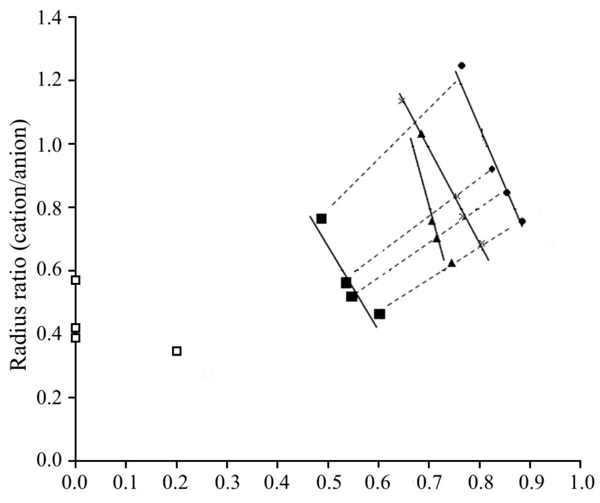

Fig. 1 Plot of estimated proportions of 6:6 coordinated ions in molten alkali halides for 4:4/6:6 mixtures ('Melting of the lithium halides' to 'Melting of the caesium halides' and 'Trends in estimated melt compositions') *vs*. radius ratios (cation/anion). For each cation (full lines) the proportion of 6:6 coordinated material showed little variation with anion change (radius ratio), □ – Li, ■ – Na, ▲ – K, × – Rb and • – Cs. Anion sizes increase downwards (interrupted lines), F, Cl, Br, I. The radius ratio for preferred 6:6 coordination stability [31] is between 0.414 to 0.732

instances of variation from the general pattern of behaviour have been mentioned above. Consideration of such deviations, through sub-classification, may have value in extending understanding, in preference to emphasizing overall similarities wherein all alkali halides are to be regarded together as a single group.

Enthalpy of fusion

Enthalpies of fusion vary from 14.65 kJ mol^{-1} for LiI to 33.62 kJ mol^{-1} for NaF (lowest and highest T_m values for the alkali halides), many being near the middle of this range [14]. Thus, ΔH_F represents only a small proportion of the lattice potential energy (Table 1). For most alkali halides, the total energy acquired on heating, 0 K to liquefaction at T_m (cumulative summation of the specific heat+latent heat), represents only about 10% that stabilizing the crystal through electrostatic bonding and ionic repulsion, estimated by the Madelung calculation [28]. ΔH_F is responsible for the changes described in 'Enthalpy of fusion (latent heat of melting)'. The electrostatic bond energy is dispersed only through volatilization at significantly higher temperatures. The specific heats of the alkali halide melts are often about 15% greater than those of the solids [33] and most boiling points are above 1500 K [37]. More importantly, the enthalpies of volatilization are significantly greater than those for fusion, many are (about) ×5 [33]. It is concluded from these relative energy values, therefore, that the bonding modifications on melting are inconsiderable. Interionic interactions are more profoundly diminished during subsequent liquid heating, and particularly, on evaporation.

Stability of coordination structures: regliq zones

Crystallographic theory, based on the efficient packing of ions of different radius ratios, predicts [31] 4:4 coordination (regular tetrahedron) when r^+/r^- is less than 0.414, 8:8 coordination when r^+/r^- is greater than 0.732 (cube) and 6:6 (regular octahedron) between these values. These structure predictions are not notably successful for the alkali halide crystals where 6:6 coordination is observed for LiBr (0.388), LiI (0.345), KF (0.964), KCl (0.762), RbF (0.875), RbCl (0.840), RbBr (0.776), CsF (0.796) and (above 742 K) CsCl (0.923). Factors in addition to the relative sizes of spheres must be important in determining solid structure. However, the comparative analysis presented here assumes, and is consistent with, the view that fusion relaxes the constraint that only the single most stable lattice form is adopted in the crystal. Thus, above the T_m, the energy available is sufficient to promote dynamic interconversions between alternative ionic arrangements so that the melt contains significant amounts of those structures shown from comparisons of packing enthalpies (Table 1) to be of comparable stabilities. The present analysis is consistent with a relaxed (wider) coordination stability 'rule' and it is now suggested that this applies more consistently to the melts.

The proportions of different structural components present in the melt are subject to control by kinetic parameters and amounts present do not necessarily correspond to equilibrium concentrations that might be predicted through thermodynamic stability calculations. Here the interconverting phases are more realistically compared with the properties and controls applicable to heterogeneous reactions involving solids [27], where the term 'concentration' has a different meaning from that used in homogeneous chemistry. Individual constituent ions, within each regliq zone, are neither equally available nor are all immediately accessible for reaction (here, structure changes may be necessary). Thus, these differ from the identical reactivities of all atoms, ions or molecules that participate in homogeneous reactions in the gas phase or in solution. Relative rates of ion transfer between different regliq zones, controlling the amounts of different forms present, are determined by the rates of loss and reception across the active irregliq interfaces and the rates of generation (nucleation)/annihilation of new regliq zones. (Some theoretical aspects of product particle formation in solid-state reactions are discussed in [27]). The limitation of ion transfers to only at and between surfaces contrasts with the conditions required for thermodynamic equilibrium in homogeneous systems where all similar ionic components possess identical reactivity.

Disordered material: irregliq zones

Formation of irregliq zones, an essential component of the set/liq model of melting, requires the generation of the disorder interfaces in the precursor crystal, an endothermic process. From the above discussions of ΔH_F magnitudes, and the proportion of this energy required for structural modification of some fraction of the melting crystal, it is estimated that irregliq formation in these melts requires (very) approximately 14 kJ mol^{-1}. This represents perhaps about half the ΔH_F (perhaps only about 1.5–2.0% of U_6) and can be used to estimate the proportion of salt that constitutes the irregliq zones. On the assumption that (on average) each ion in an irregliq zone possesses one fewer coordination link with its immediate neighbours (here most coordination numbers are reduced to 5) and that about half ΔH_F is required to form the irregliq zones, it is estimated that approximately 10% of the ions are in the irregliq domains. From an idealized representation of the matrix as regliq (ordered and equal sized) cubes, each bounded on half its sides by irregliq material of one unit cell thickness (say average 3 Å spacing), the mean linear dimension of each regliq domain is estimated to be approximately thirty unit cell edges or about 90 Å. Interestingly (and consistently) this size is closely similar to the particle dimensions that do not give effective reinforcement of diffracted X-rays (below 'roughly 20–100 Å' [26], 'The set/liq melting model: a proposed representation of the liquid at T_m', regliq). Greater disorder, or a lower average coordination number of ions in the irregliq material, would result in smaller regliq zones and higher contributions to ΔH_F. The significant result from this comparison is that this matrix of interconverting zones of crystal-type structures, maintaining much of the energy derived from ionic bonding in the crystal precursor, satisfies the observations: there is liquidity of the melt and only diffuse X-ray diffraction patterns [26]. Irregular zones, within which structural interconversions are maintained, are incapable of sustaining strain, thus conferring the fluid/flow properties that are characteristic of the liquid.

Comment

Our limited knowledge of the structures of melts in the vicinity of the T_m, restricts our ability to advance the theory of fusion because we have no adequate representational model of the changes that occur during the transformation of solid to liquid. The proposed set/liq melt model identifies the liquid structure as being (locally) closely comparable with the ionic arrays in crystalline solids because the energy and density changes that accompany melting of the alkali halides are relatively small. The dynamic character of the melt accounts for the loss of long-range order and fluidity of the liquid. The absence of sharp X-ray diffraction patterns and without a suitable experimental method for liquid structure determination, it follows that we have few insights into the internal properties of a 'cool liquid' (one close to its T_m). The sharp and discontinuous loss of 'X-ray order' is attributable here to the small size of the regliq zones generated, diffraction responses become broadened for small crystalline regions (below about 2–10 nm [26]). In the melt model proposed here, the following effects contribute to the diffuse nature of diffraction patterns. (*i*) The small sizes (and ranges of sizes) of all the regliq zones that participate in the interconverson equilibria; (*ii*) the presence of alternative regular structures that scatter and possibly rediffract X-rays; (*iii*) the less ordered domain borders, the irregliq material; (*iv*) the deviations from ionic order that result from enhanced vibrational movements in the thermally expanded lattice. Thus the local structural regularity of ionic spacing, imposed by the strong ionic forces (demonstrated by the above density and energy considerations), is not maintained over significant distances in the liquid-state with the consequent absence of sharp X-ray diffraction patterns.

From the above comparisons it appears that the lithium halides should be distinguished as a sub-set that exhibits significantly different behaviour from the properties of the other alkali halides. Recognition of such instances of apparently anomalous behaviour within the set may be of value in developing wider insights into the properties of melting. Overall, however, the set/liq model provides a representational model that is consistent with the observed changes of physical properties of this group of solids at each T_m. It may be possible to apply this model to other ionic solids and, perhaps, to a wider range of crystalline materials.

The present article proposes the dynamic set/liq model for ionic melts. Small regions of regular lattice, regliq, are separated by less ordered zones, irregliq, across which there are dynamic and rapid, mobile structural rearrangements. This is consistent with energy and density data. In the subsequent articles, Part 2 [42], this model is applied to consider the eutectic formation that occurs on melting of those binary alkali halide mixtures that contain a common ion [18]. Part 3 will discuss melting phenomena, specifically and generally, in the context of the other phase changes/rate processes that occur as the temperature of a material, initially in the form of a crystalline solid, is continually raised.

Diatomic molecule formation

Alkali halides form gaseous binary molecules stable at high temperatures [43–45]. From the bond strengths (M–X) [46], lattice potential energies (M^+A^-), anion electron affinities [47] and cation ionization potential energies [48], it is possible to calculate the enthalpy of the reaction:

$$M^+A^-(\text{crystal})\rightarrow M\text{–}X(\text{diatomic molecule})$$

Enthalpies of this reaction for the alkali halides are in the range 173–267 kJ mol^{-1} (CsF to LiF). This trend is of interest in the present context because, for a majority of these salts, there is a linear increase in T_m with the enthalpy difference (diatomic molecule – ionic crystal). The points furthest from the line on this graph include CsF, RbI and NaI (about 25, 15 and 15 kJ mol^{-1} distant respectively). The value for NaF is difficult to reconcile with the data available because the recent value given for this bond energy (519 kJ mol^{-1} [46]) is significantly larger than that listed in an earlier edition of the same Handbook (481 kJ mol^{-1}, 1981–1982, 62nd Ed.). As with the other trends identified above, the lithium halides (together with the hydride) show a separate and distinct pattern of variations.

These comparisons were included in the present analysis to determine whether it was possible that changes in the bonding properties of the ionic crystals to covalent molecule (bond: ionic→covalent) contributed significantly to the melting process. However, it seems improbable that there was any appreciable participation by covalent molecule formation, because the equilibrium proportions of diatomic molecules present (estimated from comparisons of the enthalpy of formation of the species concerned) were less than 1 ppm (M–X). The observed trend may, therefore, be identified as further manifestations of the properties of alternative bonding of these elements, but it is considered most unlikely that diatomic molecule formation is directly involved in determining the magnitude of T_m.

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