High-Pressure Melting Curve of KCl: Evidence against Lattice-Instability Theories of Melting

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We show that the large curvature in the T-P melting curve of KCl is the result of a reordering of the liquid to a more densely packed arrangement. As a result theories of melting, such as the instability model, which do not take into account the structure of the liquid fail to predict the correct pressure dependence of the melting curve.

The idea that the phenomenon of melting can be identified with an intrinsic instability of the solid has had numerous advocates.[1-3] Recently several papers have appeared on this subject.[4-8] In particular a series of papers have appeared in Physical Review Letters dealing with instability models applied to alkali halides.[4] Rigorous theory holds that melting occurs when the Gibbs free energies of the liquid and solid are equal at a given temperature and pressure. The practical drawback to this approach stems from the difficulty in the calculation of the free energy of the competing phases to sufficiently high accuracy. As a result a number of approximate models have been suggested which bypass the need to determine this troublesome quantity.[8] Some of these are the well known Lindemann law and models based on defect formation or lattice instabilities. These models have one important feature in common. They all consider the properties of only one of the phases, typically the solid, and neglect the liquid. In this regard the lattice-instability model may be regarded as the prototype of all the single-phase models.

As part of a broader program we have recently undertaken a series of Monte Carlo and lattice-dynamics calculations for the alkali halides at high pressures and temperatures. These calculations demonstrate many of the instabilities that are frequently used as melting criteria. The purpose of this paper is to show that these criteria only poorly predict the pressure dependence of melting and the reason for this is that they fail to account for liquid properties.

The pressure dependence of the alkali halide melting curves provides a severe test for the single-phase melting models. In these materials the melt is believed to undergo a continuous pressure-induced structural rearrangement from that of a relatively open structure at low pressure to one with more densely packed ordering at high pressure.[9-12] Theoretical evidence for a structural change in compressed liquid KCl was first observed by Adams[11] using the hypernetted chain equation. Hypernetted chain calculations were also made by Ross and Rogers[12] for the pair distribution functions of several shock-melted alkali halides at pressures up to several hundred kilobars. The liquid structure of an alkali halide at low pressure consists of alternating shells of positive and negative ions in which the short-range repulsions are balanced by the long-range Coulomb interaction and each atom has about four to five nearest neighbors. However, at high pressure the repulsive forces dominate with the result that the atomic packing more closely resembles that of an inert-gas fluid with twelve nearest neighbors of mixed charge.[11,12] This change in the liquid structure leads to a decrease in the volume change on melting and is responsible for the large curvature observed in the P-T (pressure-temperature) plane. In many of the alkali halides, particularly the chlorides[13] and the iodides,[14] the melting temperature of the NaCl phase appears to be approaching a maximum suggesting that the liquid density is nearly that of the solid. Kawai and Inokuti[9] and Tallon[10] have suggested that this behavior indicates that the liquid undergoes a continuous transition from a simple-cubic-like sixfold-coordinated state to a body-centered-like eightfold-coordinated structure. Figure 1 shows the melting curve for KCl measured by Pistorius.[13] Below 19 kbar KCl is in the NaCl (B1) phase and above this pressure it is in the CsCl (B2) structure. The dashed curve showing a maximum is an extrapolation of a polynomial fit made by Pistorius to the B1 melting data. The Simon-equation fit to the data, also in this figure, shows no such property. However, a melting maximum has been observed for KI.[14]

The calculations described here were carried out for KCl with the widely used Tosi-Fumi potential.[15,16] The canonical-ensemble Monte Carlo calculations
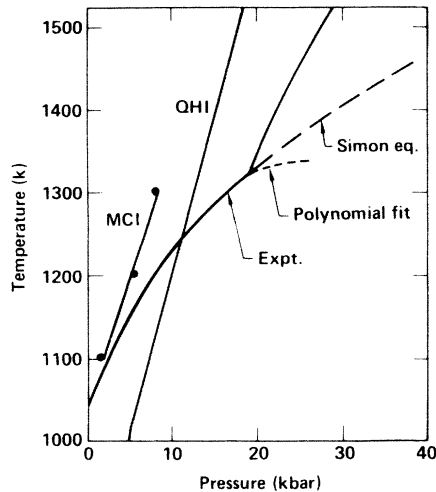

FIG. 1. The melting curve of KCl. The curve labeled "Expt." is the experimental data of Ref. 13. The remaining curves are discussed in the text.
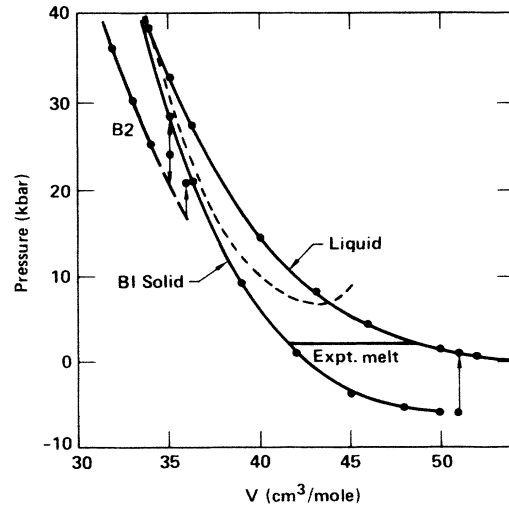

FIG. 2. Isotherms calculated for KCl at $T = 1100$ K by use of the Tosi-Fumi potential. The dots (and solid curves) were obtained with the Monte Carlo method. The dashed curve was obtained by the quasiharmonic approximation. Single arrows denote points in which the solid collapsed to a higher-pressure state. The double arrow denotes a jumping between the $B2$ and $B1$ phases.

were made with 64 particles in a box with periodic boundary conditions and all the standard procedures associated with this method. A comparison of our results with those of Dixon and Gillan[16] and also of our own with 216 particles indicates that the final pressures and reduced internal energies (U/NkT) are accurate to about 0.5 kbar and 0.05 units of U/NkT, respectively. Figure 2 shows a set of isotherms for the liquid and the $B1$ and $B2$ solid phases at $T = 1100$ K calculated with the Monte Carlo method, and a $B1$ isotherm obtained by use of quasiharmonic lattice dynamics. The normal melting temperature of KCl is 1043 K. The figure contains several noteworthy features. First, both sets of calculations show evidence of an instability in the $B1$ phase. The lattice-dynamics results (dashed curve) show the type of instability Herzfeld and Goeppert Mayer,[1] Kane,[2] and more recently Boyer[4] have associated with melting. This is a thermoelastic instability in which the crystal becomes unstable because of a vanishing of the isothermal bulk modulus. In the case of the Monte Carlo isotherm an expansion of the solid to sufficiently large volume results in a collapse of the $B1$ solid to a liquid at a pressure of 1.6 kbar. This is very near the melting pressure of 2.2 kbar reported at this temperature. These will be referred to respectively as the quasiharmonic (QHI) and Monte Carlo (MCI) instabilities. But neither of these is a thermodynamic transition between states of equal free energy. They represent instabilities of particular models. If we identify these with melting then a series of similar calculations made at several temperatures predict the lines shown in Fig. 1 along with the experimental curve. In both cases the predicted melting curves are linear and in qualitative disagreement with the measurements which exhibit a

large negative curvature. The Monte Carlo calculations in Fig. 2 also show that the $B2$ phase becomes unstable below about 25 kbar, in good agreement with the observed transition at 19 kbar. This feature is being pursued in a separate study. In this paper we restrict ourselves to a discussion of melting in the $B1$ phase. A second noteworthy feature demonstrated in Fig. 2 is the steady decrease in the volume change on going from the solid to liquid as the pressure is increased. This is a consequence of the structural reordering of the liquid into a more densely packed arrangement.

A third feature worth noting in Fig. 2 is the large discrepancy between the pressures calculated for the solid by the Monte Carlo procedure and quasiharmonic lattice dynamics. Shukla et al.[17] have shown, with the use of self-consistent average-phonon theory, that the quasiharmonic model calculates pressures that are too high because of the omission of anharmonic terms. These terms are included in the Monte Carlo calculations. But including anharmonic terms only shifts the pressure scale and the instability model still fails to predict a qualitatively correct melting curve.

It would be desirable to carry out a rigorous calculation of the melting curve in order to demonstrate that the curvature in the P-T plane is directly attributable to the change in the liquid structure. At the present time such a calculation would represent an enormous effort and would be a questionable undertaking given the uncertainties in the actual intermolecular forces. However, a useful estimate for the pressure depen-
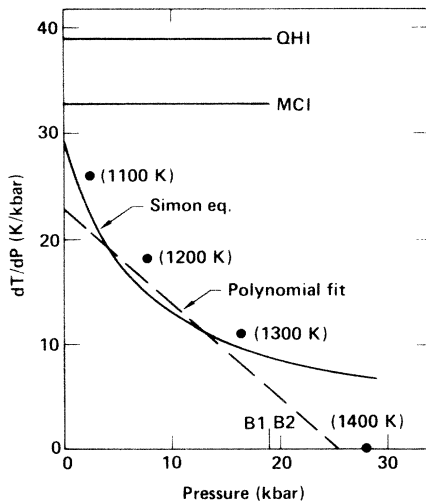
FIG. 3. The values of dT/dP along the melting curve vs pressure determined experimentally (by the Simon equation and polynomial fits to data) and by the Monte Carlo isotherms by means of the Clausius-Clapeyron equation (circles). MCI and QHI are melting lines predicted by the instability criteria discussed in the text.

dence of dT/dP along the melting curve can be obtained from the Clausius-Clapeyron equation with use of the results of the Monte Carlo calculations. This equation is written as

$$dT/dP = \Delta V/\Delta S,$$

where ΔV and ΔS are respectively the volume and entropy changes on melting. Solid and liquid isotherms were calculated at several temperatures and the values of ΔV and ΔS (actually $\Delta H/T$) were determined by taking the difference in volume and enthalpy between the two isotherms at the experimentally determined melting pressure. The calculated values of dT/dP are compared in Fig. 3 to the derivatives of the Simon equation and the polynomial function which Pistorius used to fit the P-T data. The Monte Carlo results are in satisfactory agreement with the measured values and in particular exhibit the same pressure dependence. Most of the disagreement comes from the Tosi-Fumi potential which predicts pressures that are too high. In contrast, the instability models predict a constant value for dT/dP which is not consistent with the experiment.

Figure 4(a) shows ΔV decreasing with increasing melting temperature. Since the variation in $\Delta S/Nk$ is small [Fig. 4(b)] the decrease in dT/dP must be due to ΔV which is predicted to become zero near 1400 K. A set of calculations made at this temperature shows the liquid and $B1$ isotherms crossing at 28 kbar where both have the same density. But $B2$ is the stable phase at this pressure and the predicted maximum is not observed. The point at 28 kbar and 1400 K has
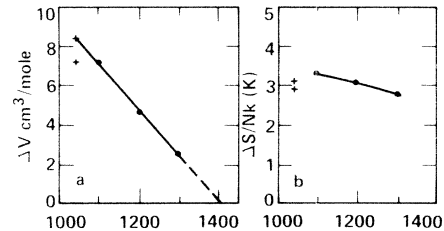

FIG. 4. Calculated (a) volume change (ΔV) and (b) entropy change ($\Delta S/Nk$) in reduced units, vs melting temperature. The reported experimental values (Ref. 13) are indicated by plusses.

been used in Fig. 3 to tie down the intercept on the pressure axis for the metastable $B1$ melting curve.

Figure 5 shows the total pair distribution function $g(r/a)$ for KCl calculated in the liquid at several temperatures along the experimental melting curve. Here $g = (g_{++} + g_{+-})/2$, and g_{++} and g_{+-} are the partial functions. The interatomic separation is expressed in reduced units of r/a where $a = (3V/4\pi N)^{1/3}$. At the normal melting point of 1043 K the first-neighbor peak consisting mainly of oppositely charged ions and the second-neighbor peak of like-charged ions are both clearly distinguishable. The total number of first-shell neighbors at this temperature is 4.1 with about 4.0 being of opposite charge. As the pressure is increased the position of the first peak shifts to larger separations, as is to be expected if the coordination number were increasing. In addition, the first two peaks begin to coalesce into a single and more densely packed nearest-neighbor shell with an increase of mixed charge. At 1300 K there are 4.6 atoms in the nearest-neighbor shell of which 4.3 are oppositely charged. Unfortunately the $B1$ phase is not stable to much higher temperatures. But the $g(r/a)$ for the fluid at
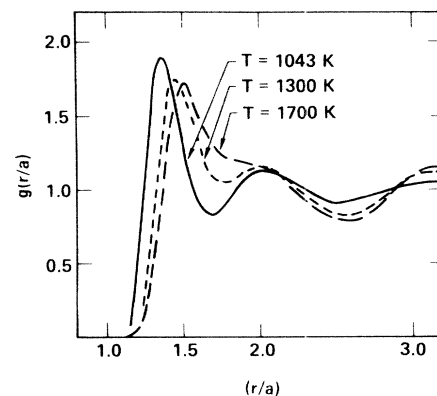

FIG. 5. Total pair distribution functions, $g(r/a)$, calculated at several temperatures along the experimental melt line. At 1700 K the liquid is in equilibrium with the $B2$ phase.

1700 K in equilibrium with the $B2$ phase gives a value of 5.1 for the number of nearest neighbors of which 4.7 are oppositely charged.

The melting behavior of the alkali halides stands in sharp contrast to the situation with relatively simple fluids such as argon and metals such as sodium and aluminum. In these materials the atoms may be approximated as hard spheres or as particles interacting through purely repulsive inverse-power potentials. It can be shown that for such idealized systems there is only a single characteristic isotherm and all the properties including those along the melting lines scale in accordance with the temperature and density in terms of a single reduced variable.[18,19] This means that the arrangement of atoms in the liquid or in the solid is the same at all pressures along the melting curve. As a result the instability and melting points will always have the same pressure dependence. This scaling also forms the basis of the Lindemann melting law. However, in the case of the alkali halides the pressure-induced structural reorganization of the fluid prevents any scaling and thus provides a more stringent test for any theory of melting which neglects the properties of the fluid.

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