

Melting temperatures and possible precursor plastic phases of CCl_4 and GeI_4 as a function of pressure

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Abstract

The motivation for the present study is to be found in the recent experiments of Fuchizaki and Hamaya [1] on GeI_4 . They observed a rapid increase in the melting temperature T_m in going from atmospheric pressure to $p \approx 2.6$ GPa. T_m was found to be largely independent of pressure above this value.

In this paper, heuristic arguments are presented to support the idea that until some critical pressure, a crystalline phase of SnI_4 , CCl_4 and GeI_4 molecular solids melts into a low density liquid. However, at this critical pressure, a phase boundary intersects $T_m(p)$, separating a low density liquid phase from a high density liquid. The new phase boundary is between the crystal and an amorphous molecular solid with increasing polymerisation as the pressure is increased.

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I. BACKGROUND AND OUTLINE

A decade or so ago, Tozzini, March and Tosi [2] considered the melting of solid N₂ heuristically, together with the precursor transition to a plastic phase. A parameterised model proposed by Pople and Karasz [3] was employed, and led to a reasonably plausible interpretation of the experimental data.

We have reopened this area, motivated by the very recent experiments of Fuchizaki and Hamaya (FH) [1] on GeI₄. Their Fig 8, in particular shows a rather rapid increase of the melting temperature T_m from atmospheric pressure to $p \approx 2.6$ GPa, from about 500 K to over 1000 K. After that, however, it is found experimentally that $T_m = 1140 \pm 20$ K, essentially independent of pressure, p .

The above experimental study, plus the earlier work of Tozzini et al [2] has led us first to consider the crystalline phase (CP) of AX₄ molecular solids (where A is a group-4 element and X is a halogen) under pressure.

The outline of the present article is then as follows. In Section 2 below, we outline some of the key experimental findings that have been reported for the AX₄ molecular solids under pressure. In Section 3, we give a heuristic treatment of (a) T_m as a function of p specifically from the CP of AX₄ molecular solids and (b) the precursor phase transition after which orientational degrees of freedom of the molecules, frozen out at the lower temperatures, are suddenly released to yield a plastic phase. Finally, Section 4 records the conclusions from the present work, together with some suggestions for further study, both experimental and theoretical, that should prove fruitful.

II. AX₄ MOLECULAR SOLIDS UNDER PRESSURE

Pasternak et al [4] carried out a detailed X-ray and Mossbauer spectroscopy study of pressure amorphized GeI₄ and concluded that the onset of structural disorder at about 12 GPa was accompanied by a molecular association process. Their results suggest a gradual growth of a disordered (GeI₄)_n polymer phase characterised by an increase in the Ge-I bond

lengths and a delocalization of the electrons by transfer from the iodine p -valence band to the $s - p$ bands of Ge.

Fujii et al [5] used X-ray spectroscopy to study the structure of SnI_4 under pressure. They found that there was a novel crystal to amorphous transition at about 8 GPa. The cubic lattice with 8 molecules per unit cell is transformed to an amorphous state with randomly packed SnI_4 tetrahedral molecules. A Raman study by Sugai [6] showed that these molecules form dimers in the amorphous phase. Electrical resistivity measurements show that this pressure induced amorphization is accompanied by a drastic reduction in its resistivity suggesting metallization under high pressure.

The insulator to metal transition was previously reported for both GeI_4 and SnI_4 [7]. Chen et al [7] invoked a model based on the formation of I-I bonds which resulted in polymerization into SnI_4 chains to explain both the amorphization and metallization under high pressure.

In their study of the melting curve of GeI_4 , FH [1] found that they were able to fit the data for the melting temperature T_m as a function of pressure, p , below 3 GPa with the Simon equation

$$\frac{p}{p_0} = \left(\frac{T_m}{T_{m0}} \right)^{c_S}$$

where p_0 and T_{m0} are values at the reference state and c_S is a constant, However, this equation was found not to hold true for pressures above 3 GPa. They also looked to see if the melting curve could be fitted by the Kechin equation [8] which gives an approximate formula for the reduced melting temperature at pressure p , $t_m(p) = T_m(p)/T_m(p = 0)$ as

$$t_m(p) = \left(1 + \frac{p}{a} \right)^b e^{-cp} \quad (1)$$

They found that while it was not possible to fit the data over the entire pressure range investigated, for pressures $p < 2.6$ GPa, there was a good fit to the data. In Figure 1, we have replotted their experimental values for $p < 2.6$ GPa together with a best fit Kechin equation with values $a = 0.606 \text{ GPa}^{-1}$, $b = 0.809$ and $c = 0.156 \text{ GPa}^{-1}$. This confirms the view that below this critical pressure, the melting curve is well described by both the Simon and Kechin equations.

However, for pressures above this critical pressure, the data is not well described by these equations. FH also attempted to fit the melting curve with other models of melting, but were not able to reproduce the strong non-linear feature in the observed melting curve. The

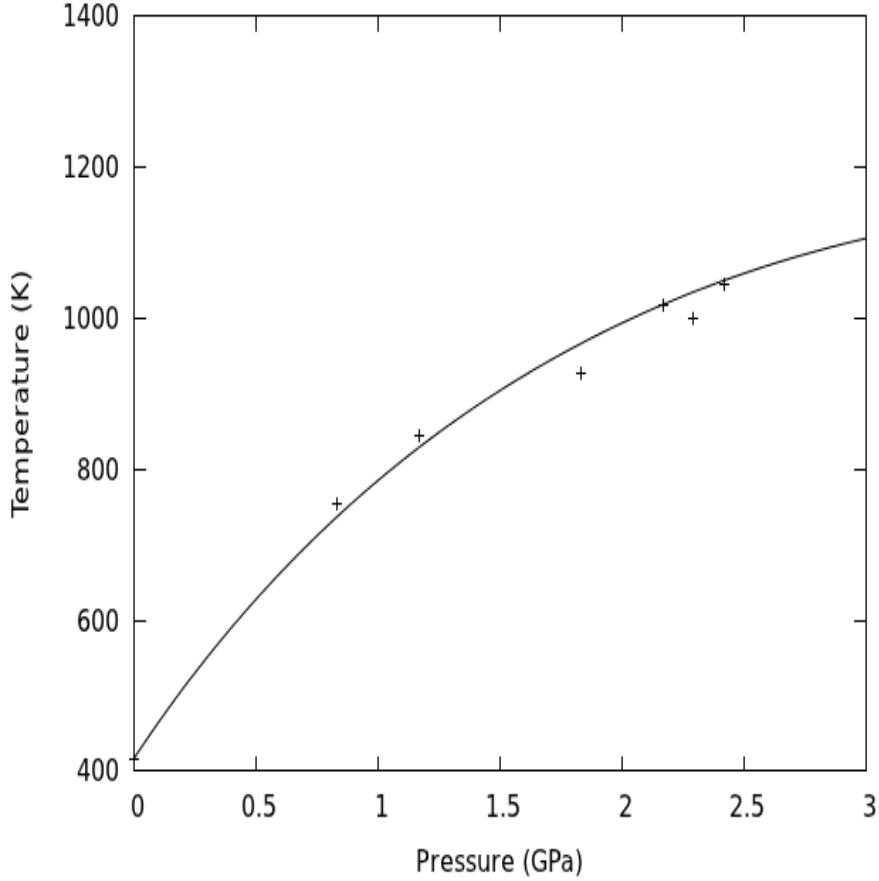


FIG. 1: The melting temperature against pressure for GeI_4 as measured by FH (plus signs) together with the best Kechin equation fit (full curve).

other significant finding of FH was the existence of two liquid states where the transition between the two characterised by a change in the density.

III. A POLYMERIC MODEL FOR THE AX_4 MOLECULAR SOLIDS UNDER PRESSURE

In order to build a structural model of the AX_4 molecular solids under pressure, it is necessary that the model takes account of all the experimental observations, These include the presence of possibly two liquid states, an amorphous state which shows increased polymerisation with pressure, the metallization under pressure and the near constant melting temperature for pressures greater than some critical pressure. The value of the critical pressure is dependent on the specifics of the molecular solid.

In their x-ray diffraction study of pressure-induced structural changes of intermediate-range order in poly(4-methyl-1-pentene) (P4MP1) melts, Chiba et al [9] found that the first sharp diffraction peak (FSDP) intensity $I(\text{FSDP})$ decreased with pressure. Additionally, the ratio of $I(\text{FSDP})$ to the intensity of the second peak also decreased sharply under pressure. Their analysis pointed to a structural change corresponding to a change in the intermediate range order. This intermediate range was assigned to be between short range discrete chemical bonds and long range crystalline order. They also found that the low pressure solids had high compressibilities.

It is generally agreed that in polymers, the $I(\text{FSDP})$ is a measure of the polymer backbone-backbone correlations. Thus, a decrease in $I(\text{FSDP})$ points a disordering of these backbone-backbone correlations and a shift to higher momentum transfers. This led Chiba et al [9] to construct a model of polymer chains such that the polymer backbones were separated by void spaces filled with the polymer side chains. At low pressures, the void space between the backbone chains is quite large and consequently the resulting loose structure is highly compressible.

We propose a similar structural model for the AX_4 molecular solids under pressure. As the crystalline molecular solid is pressurised, there is a breakdown of the structural order as found by Fujii et al for SnI_4 [5]. This is also consistent with the investigations of Purskii [10] et al on the pressure dependence of the thermal conductivity of CCl_4 . They found that the phonon contribution to the thermal resistance decreases as the rotational motion of the molecules attain more freedom under pressure.

Then as the pressure is increased further, the X-X bonds between adjacent AX_4 molecules become stronger and the amorphous structure comprises disordered AX_4 molecules in equilibrium with the polymer chains (Figure 2a), As the pressure is increased again, the ratio of polymer chains to the free molecules increases until all the isolated molecules become polymerised. The solid-liquid transition on increasing temperature results in the two liquid phases differentiated by density.

The melting curve found by FH now be explained in terms of melting from two phases. At low pressures ($< 3 \text{ GPa}$) which is well below the amorphous transition pressure, the melting is from a crystalline phase and is well described by the Simon equation. This is because the solid transforms to a liquid of AX_4 molecules. The increase in the melting temperature at higher pressures arises from the decrease in volume which in turn makes it harder to break

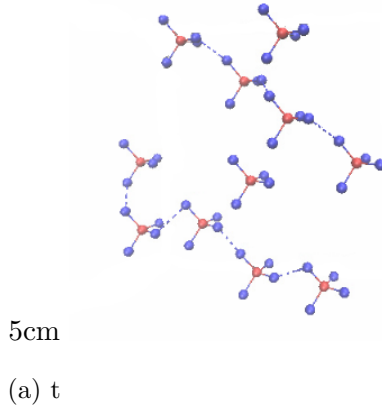


FIG. 2: (a)



FIG. 3: (b)

FIG. 4: Schematic of the amorphous structure of the AX_4 molecular solids. (a) shows the polymerisation of the AX_4 monomers with isolated AX_4 molecules occupying the void space between polymers, and (b) shows the backbone structure of the fully polymerised structure.

the inter-molecular bonds to form a liquid. However, at higher pressures, the solid becomes a polymeric solid which transforms to a liquid at roughly the same temperature, independent of pressure. The melting temperature is determined solely by the energy required to break the inter-polymer bonds. This energy is independent of pressure and results in the flattening of the melting temperature curve observed by FH. The ensuing polymerised liquid state is of higher density than the liquid comprised of AX_4 molecules. Based on these observations, we propose a phase diagram for the AX_4 molecular solids and this is schematically shown in Figure 3.

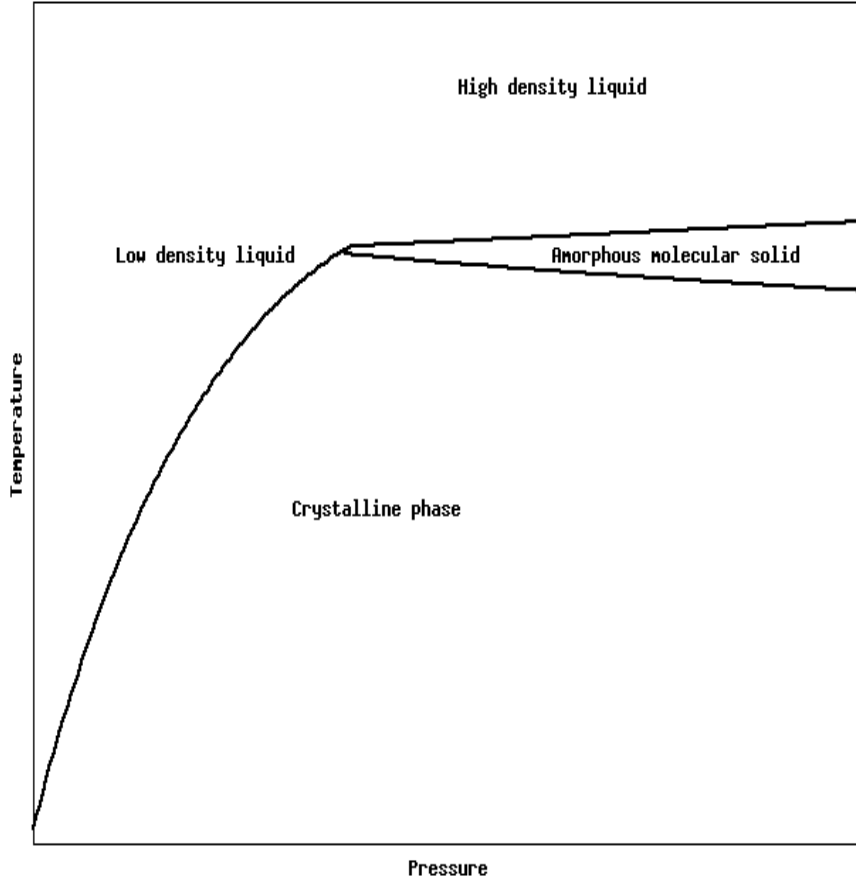


FIG. 5: Proposed phase diagram for the AX_4 solids.

IV. SUMMARY AND FUTURE DIRECTIONS

Our main conclusions are summarised in the proposed phase diagram for AX_4 molecular solids in Figure 3. As p is increased beyond some critical pressure, a new phase boundary is inserted separating the crystal from an amorphous molecular solid which we conjecture would show increased polymerisation as p extends beyond this critical pressure. We advocate that further experiments to confirm this increased polymerisation in both the amorphous solid and in the high density liquid be carried out. In parallel, computer simulation studies investigating the polymerisation under pressure is a worthwhile endeavour.

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