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THERMODYNAMICS AND STRUCTURE OF UNDERCOOLED LIQUID METALS

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Résumé - On étudie l'évolution de métaux purs surfondu depuis la température de fusion $T_M$ jusqu'à 0.5$T_M$. Par la théorie du pseudopotentiel et l'ORPA, on prédit une accentuation des particularités structurales. Le rôle déterminant des interactions à moyenne et longue portée est mis en avant aussi bien dans l'état surfondu que dans l'état amorphe de Ga, Sn, Bi.

Abstract - We study the structural evolution of undercooled pure metals from the melting temperature $T_M$ to 0.5$T_M$. By means of the pseudopotential theory and ORPA we predict an increase of the structural trends. The prime importance of the intermediate and long ranged interactions is underlined to understand the undercooled state as well as amorphous state of Ga, Sn, Bi.

I - INTRODUCTION

It is striking that the pure metals which can be obtained at deep level of undercooling: Ga, Hg, Sn, Bi/1,2/ have a non hard-sphere-like liquid structure, since their structure factor $S(q)$ and pair correlation function $g(r)$ exhibit special distortion. A good link between the effective interionic pair potential $V(r)$ and the structure can be realized by thermodynamic perturbation theories such as the ORPA /3/ which is suitable for liquid metals /4/. Recently, Hafner and Kahl /5/ have fairly classified all the structural trends observed in liquid metals in terms of the systematic variations of $V(r)$ with electron density and local pseudopotential. However, a more quantitative study of the thermodynamics and structure of the previous metals needs the use of non local pseudopotential /4,6/. Thus, specific effects due to the long ranged part of $V(r)$ can be pointed out on the temperature derivative of the resistivity (TDR) /7/.

In this work, we intend to examine if the pseudopotential and the ORPA formalism can works well below the melting temperature $T_M$. The ultimate temperatures which have been reached in the undercooled droplets of metal, just before their spontaneous crystallization, are close to 0.5$T_M$ /1,7/. Several theories have been presented to define the structural and thermodynamical behaviour near this experimental limit /8,9/. Few measurements have been done, and they principally concern the structure of Ga/1/ and the heat capacity $C_p$ at constant pressure /2/. So we concentrate ourselves on these properties and on the TDR since non linear variations for $T < T_M$ have been predicted by Pokorny and Aström /10/, as a consequence of their measurements for $T > T_M$. As a matter of comparison with Ga, Sn, Bi we also consider hypothetical states of undercooled Al.

II - SHORT DESCRIPTION OF THE MODELS

Before considering the undercooled liquid, we have defined a representation of the pseudopotential which allows a good description of the normal liquid in the range $T_M - 1.5T_M$. We follow the procedure and references given in /4/. The bare-ion pseudopotential $v_{ps}$ is represented by the non show-local model of shaw. We define the exchange correlation terms as Vashishta and Singwi. One important point is that we do not include effective masses in the case of Sn and Bi since such masses give an unrealis-
tic pair potential for these two metals. The calculation of the structure and thermo-
dynamics is done from the ORPA. The reference system is the fluid of hard-sphere (HS),
which diameter $\sigma$ is defined from the repulsive core of $V(r)$. Then the correlation
function $C_\sigma(r)$ induced by the oscillatory part of the potential, $V_a(r)$, is calculated
in terms of an optimized potential $V_a^<(r)$. This means that the usual RPA expansion
$C_\sigma(r) = -V_a(r)/k_BT$ for $r > \sigma$ is optimized for $r < \sigma$ so that the pair correlation func-
tion $g(r)$ is effectively zero for distances $r < \sigma$. Therefore the modified structure
factor is expressed from the hard-sphere one $S_\sigma(q)$ and $V_a^<(q)$.

$$S(q) = S_\sigma(q) \left[ 1 - V_a^<(q) S_\sigma(q)/k_BT \right]^{-1}$$ (1)

For simplicity, we do not discuss the supplementary soft core correction to (1) which
permits the adjustment of $\sigma$. However, this correction is considered in our calcu-
lation.

The variation of the liquid density with temperature is assumed to follow the linear
parametrization of Crawley /1/. The change of $S(q)$ depends on temperature, through (1)
and on the density. The density dependence is explicit in the packing fraction of the
HS, but it is implicit in $V(r)$ through the modifications of the screening length, the
Friedel wavelength and the core parameters of vps /5/. Here, this variations are
fully taken into account. In fig.1, we have represented $V(r)/k_BT$ at $T = T_M$ and $0.5T_M$.
We see that the undercooling with favor the emergence of the long ranged correlations
relatively more than those of the first attractive well region.

III - RESULTS AND DISCUSSION

The evolution of the structures from $T_M$ to $0.5T_M$ are presented in fig.2. Considering
first Ga, we obtain a moderate quantitative agreement with the experiment at $T_M$ and
$0.5T_M$. This is not surprising since we have performed ab initio calculation, i.e.
without adjustment of the core radius $R$ of $r_{HS}$, to better fit the data. The important
result is that the model reproduces the change of $S(q)$ with temperature, i.e. the in-
crease of the principal peak and of its shoulder as well as the evolution of the profile
of $g(r)$. In particular, all the special wiggles on $g(r)$, although too much pronounced
in the model are placed exactly where similar wiggles are found in the pure amorphous
$Ga$ or in the corresponding quasicrystalline model of $ß-Ga$. $ß-Ga$ is the metastable
structure in which the deep undercooled liquid prefers to crystallize /12/.

In the case of Al, no tendancy to any asymetry in $S(q)$ appears at low temperature
(fig.2b). This would have been expected from the increasing influence of the Friedel
oscillations alone. In fact, what we observe is in full agreement with the trends
predicted by Hafner and Kahl in terms of the variation of $r_C/r_S$ (the ratio of the
ionic core radius to the electronic density radius). In the case of the light trivalents, an increase of $r_c/r_s$ favors a symmetrical shape of $S(q)$. When undercooling, $r_c/r_s$ increases by 0.5% in Ga but 2% in Al. In the latter metal this variation counterbalances the influence of the Friedel oscillations. The hard-sphere like behaviour of Al at $0.5T_M$ is also confirmed in fig.2C. The theoretical $g(r)$ is indeed very close to the pure hard sphere calculation of (1) by neglecting the influence of $V_f(r)$. The asymmetrical second peak at $r = 8$ a.u. is that of the HS one at high packing fraction /13/, and is reminiscent of the random close packing of spheres.

![Fig.2](image_url)

**Fig.2** - Structure factors at $T_M(a)$, $0.5T_M(b)$ and pair correlation functions at $0.5T_M(c)$. Theory (full line). Experiments near $T_M$ Bi, Sn, Ga, Al /1,18/ (crosses x). Experiments near $0.5T_M$: Ga /1/ (crosses x). Amorphous Bi and Ga at 4K /12/ (triangles). Simulation of a hard sphere glass /14/ (crosses +).

However, such an effect is less pronounced than in the Bernal model or in the simulation of the glassy state of the HS /14/. For Al and Ga at $T = 0.5T_M$ we obtain for the underlying HS $\eta = 0.54$ and $\eta = 0.57$. It is also possible that in this range of $\eta$, the HS model that we use is less accurate (the Verlet-Weis model of HS is fitted to Monte Carlo results in an range $\eta < 0.5$). Whatever it may be, our result exhibits the preferred arrangement of the hypothetical undercooled Al towards the random close packing. In the case of Sn and Bi we equally obtain a specific evolution of the structure. Moreover we need not to speculate about the accuracy of the HS system since the packing fraction obtained are respectively 0.40 and 0.46. One remarkable result is the strong analogy between undercooled Bi at $0.5T_M$ and pure amorphous Bi at 4K (fig.2c).

**Trends in $C_p$**
To obtain $C_p$, we calculate the entropy $S(T,P)$ along the line of the constant normal pressure in the phase diagram. Then we calculate the mean derivative of $S$ vs temperature...
ture by large steps of 0.1T_M to obtain stable results for Cp. The values of Cp, and of the entropy S_E in excess from the ideal gas value are given in table 1 and fig.3 in units of the Boltzmann constant k_B.

<table>
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<th>Ga</th>
<th>Sn</th>
<th>Bi</th>
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<td>4.0</td>
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<td>(4.1)</td>
<td>(3.7)</td>
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C_p | Al  | Ga  | Sn  | Bi  |
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<td>(3.4)</td>
<td>(3.4)</td>
<td>(3.6)</td>
<td>3.7</td>
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</table>

Table 1: Calculated Excess entropy and heat capacity at T_M. The experimental values are in parenthesis and from /15/.

The results are very convenient for Al, while the agreement with experiment decreases as we go toward the heavy polyvalents. Although the pair forces model is certainly incomplete to explain all the configurational change in the undercooled state, we see that the rise in Cp observed in /2/ is approximatively reproduced (fig.3).

Resistivities
The resistivity $\rho$ and its derivative at the melting point are reported table 2. To point out the effect of the structural evolution when undercooling we also calculate the resistivity in the soft sphere approximation, where the effect of $V_a(r)$ is neglected /7/. We can observe in fig.4 that the change of $\Delta \rho$ due to $V_a(r)$ increases from Al to Bi in different ways. In the range 0.5 - 1.5T_M $\Delta T$ the TDR is almost constant in Al. In Ga we obtain a small maximum near T_M, in qualitative agreement with /10/, but no such maximum appears in Sn as suggested in /10/. The main effect that we expect will be a rapid decrease of the TDR at deep level of undercooling due to the progressive departure from the HS-like structure.

<table>
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<tr>
<th>$\rho$ nc/m</th>
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<th>Sn</th>
<th>Bi</th>
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<td>26.5</td>
<td>49.1</td>
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<td>(22.8)</td>
<td>(26)</td>
<td>(47.6)</td>
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1/\rho | Al  | Ga  | Sn  | Bi  |
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<td>(7)</td>
<td>(7.7)</td>
<td>(4.8)</td>
<td>(4)</td>
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</table>

Table 2: Resistivity and temperature coefficient for $T = T_M$. The experimental values are in parenthesis and from /10,17/.

Fig.3 - Heat capacity Vs temperature. Theory (full line). Experiments Bi/2/ (circles) Sn/2/ (crosses), Ga/16/ (triangle).

Fig.4 - TDR theory (full line). The dashed line corresponds to the soft sphere model.
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