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THERMODYNAMICS AND STRUCTURE OF UNDERCOOLED LIQUID METALS

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Résumé - On étudie l'évolution de métaux purs surfondus depuis la température de fusion T_M jusqu'à $0.5T_M$. Par la théorie du pseudopotentiel et l'ORPA, on prévoit 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 $0.5T_M$. 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 work 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 $0.5T_M$ /1,2/. 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 /6/. 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 thermodynamics is done from the ORPA. The reference system is the fluid of hard-sphere (HS), which diameter σ is defined from the repulsive core of $V(r)$. Then the correlation function $C_a(r)$ 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 $C_a(r) = -V_a(r)/k_B T$ for $r > \sigma$ is optimized for $r < \sigma$ so that the pair correlation function $g(r)$ is effectively zero for distances $r < \sigma$. Therefore the modified structure factor is expressed from the hard-sphere one $S_\sigma(q)$ and $V_a^{**}(q)$.

$$S(q) = S_\sigma(q) [1 - V_a^{**}(q) S_\sigma(q)/k_B T]^{-1} \quad (1)$$

For simplicity, we do not discuss the supplementary soft core correction to (1) which permits the adjustment of σ . However, this correction is considered in our calculation.

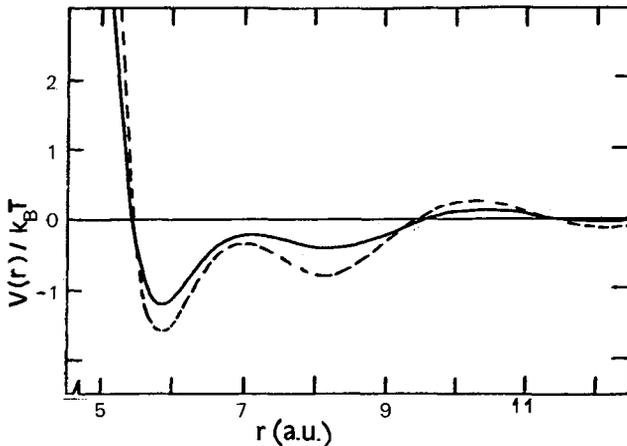


Fig.1 - Pair potential of Bi (in units of $k_B T$), at melting temperature T_M (full line) and at $0.5T_M$ (dashed line).

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, these variations are fully taken into account. In fig.1, we have represented $V(r)/k_B T$ at $T = T_M$ and $0.5T_M$. We see that the undercooling favors the emergence of the long ranged correlations relatively more than those of the first attractive well region. Once $S(q)$ and its real space equivalent $g(r)$ are obtained, the computation of the excess free energy, of the heat capacity and of the resistivity (through the Ziman formula) are straight forward.

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_1 of v_{DS} , to better fit the data. The important result is that the model reproduces the change of $S(q)$ with temperature, i.e. the increase 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 β -Ga. β -Ga is the metastable structure in which the deep undercooled liquid prefers to crystallize /12/. In the case of Al, no tendency to any asymmetry 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 trivalent, 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 counter balances 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 $V_a(r)$. 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.

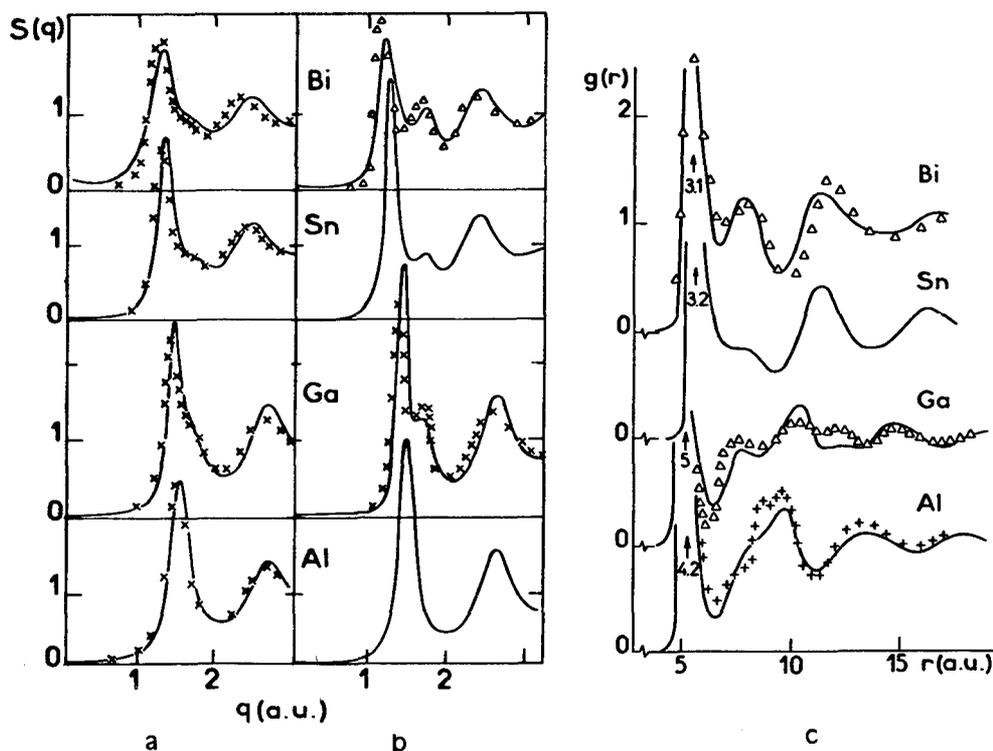


Fig.2 - Structure factors at T_M (a), $0.5T_M$ (b) and pair correlation functions at $0.5T_M$ (c). Theory(full line). Experiments near T_M Bi, Sn, Ga, Al /1,18/ (crosses x). Experiments near $0.5T_M$: Ga/1/ (crosses x). Amorphous Bi and Ga at 4K /12/ (triangles) Simulation of a hard sphere glass /14/ (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 η , the HS model that we use is less accurate (the Verlet-Weis model of HS is fitted to Monte Carlo results in a range $\eta < 0.5$). Whatever it may be, our result exhibits the preferred arrangement of the hypotheticalal 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 tempera-

ture by large steps of $0.1T_M$ to obtain stable results for C_p . The values of C_p , 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 .

	Al	Ga	Sn	Bi
$-S_E$	3.6 (3.6)	4.0 (4.6)	3.5 (4.1)	2.3 (3.7)
C_p	3.8 (3.4)	2.6 (3.4)	3 (3.6)	2.4 (3.7)

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

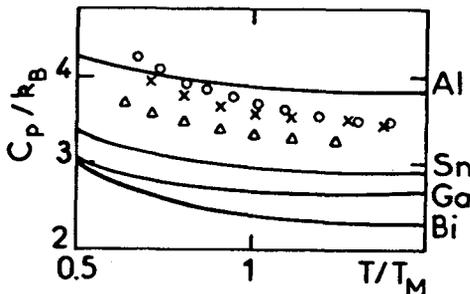


Fig.3 - Heat capacity Vs temperature. theory (full line). Experiments Bi/2/ (circles) Sn/2/ (crosses), Ga/16/(triangles)

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 C_p observed in /2/ is approximately reproduced (fig.3).

Resistivities

The resistivity ρ 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 $\frac{\partial \rho}{\partial T}$ due to $V_a(r)$ increases from Al to Bi in different ways. In the range $0.5 - 1.5T_M$ $\frac{\partial T}{\partial T}$ 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.

	Al	Ga	Sn	Bi
ρ	16.7	26.5	49.1	76.5
$\mu\Omega\text{cm}$	(22.8)	(26)	(47.6)	(129.1)
$\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$	5 (7)	5.7 (7.7)	2.9 (4.8)	2.5 (4)

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

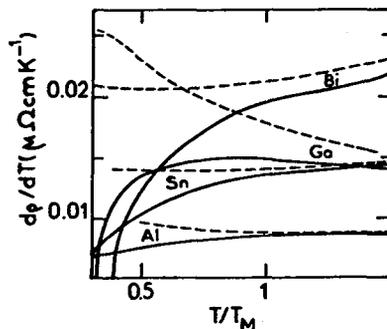


Fig.4 - TDR theory (full line) The dashed line corresponds to the soft sphere model.

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