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AN INTRODUCTION TO THE STUDY OF LIQUID METALS AND ALLOYS

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Résumé. — On présente une courte revue des propriétés électriques des métaux et des alliages liquides en se référant particulièrement aux alliages à base d'un métal alcalin et aux alcalins terreux liquides. Puis on se concentre sur des problèmes structuraux associés à des alliages liquides, particulièrement ceux dans lesquels une transition métal-semiconducteur se produit graduellement lorsque la composition change. Des résultats expérimentaux sont confrontés à des modèles structuraux qui impliquent la notion d'amas. On proposera un rapport explicite entre les propriétés structurales d'une part et les propriétés électroniques d'autre part.

Abstract. — A brief review is given of the electrical properties of liquid metals and alloys with special reference to alkali metal based alloys and the liquid alkaline earths. Attention is then focussed on structural problems associated with liquid alloys particularly those in which a gradual transition occurs from metallic to semiconducting behaviour as the composition is varied. Experimental evidence will be presented against structural models which involve the notion of clusters. An explicit connection between the structural properties on the one hand and the electronic properties on the other will be suggested.

1. The electrical properties of pure liquid metals. —

1.1 SIMPLE LIQUID METALS. — The theoretical and experimental situation for simple liquid metals (i. e. those in which d- or f-like resonance behaviour is well removed from the Fermi energy E_F) has not materially changed since the review article by Cusack [1] was written a decade ago. Tentative generalisations made at that time have, with the passage of time, become generally accepted. The nearly free electron picture of liquid metals as evidenced by Hall coefficient, electrical resistivity and optical studies, is now well established and for an up-to-date review of the present situation the reader is referred to the book by Faber [2]. The Ziman [3] formula for the electrical resistivity, involving as it does the pseudopotential and the liquid structure factor, has received considerable experimental support in recent years.

1.2 LIQUID ALKALINE EARTH METALS. — The group IIa elements (Mg, Ca, Sr and Ba) are important because they represent, in the condensed states, metals which are precursors of the transition series. The effect of the empty d-states above E_F will therefore begin to affect the electrical properties and to this end a study of the resistivity and thermoelectric power of liquid alkaline earth metals has now been completed (Van Zytveld, Enderby and Collings [4]). The resistivity measurements were interpreted in terms of resonance scattering from the vacant d-states. The

thermoelectric power results indicated the increasing role of the energy dependence of the pseudopotential as one proceeds from Mg to Ba. Calculations by Ratti and Evans [5] in which the effect of the d-bands is incorporated into an energy dependent pseudopotential confirm this trend.

2. The electrical properties of liquid alloys. — In 1964 Faber and Ziman [6] showed that if scattering of electrons in a binary alloy is treated in Born approximation, the resistivity can again be evaluated in terms of pseudopotentials and structure factors.

Let us define a generalised form factor $F(q)$ given by :

$$F(q) = |w_1|^2 [c(1-c) + c^2 a_{11}] + |w_2|^2 [c(1-c) + (1-c)^2 a_{22}] + 2 w_1 w_2 c(1-c) (a_{12} - 1).$$

Here the pseudopotentials of the two components are written as w_1 and w_2 , while c is the atomic fraction of component 1 ; a_{11} , a_{22} and a_{12} represent the three partial structure factors, the definition and determination of which will be discussed in paragraph 3. It then follows that the conductivity σ of a binary liquid alloy can be expressed as

$$\sigma = \left\{ \frac{3 \pi^2}{e^2 \hbar v_F^2} \Omega \langle F(q) \rangle \right\}^{-1}$$

where

$$\langle F \rangle = \int_0^{2k_F} F(q) q^3 dq$$

v_F and k_F are respectively the Fermi velocity and Fermi wave number and Ω is the atomic volume.

A thoroughgoing comparison of theory and experiment is not in general possible because information about the partial structure factors $a_{\alpha\beta}$ is limited. However when $a_{\alpha\beta}$ can be plausibly assumed to be independent of c (e. g., liquid Au-Ag) or determined directly (e. g. liquid Cu-Sn) the experimental transport data for a certain class of liquid alloys are in excellent agreement with those predicted by the Faber-Ziman theory. Such alloys are characterised by conductivities greater than $\sim 3\,000\ \Omega^{-1}\text{cm}^{-1}$, thermopowers (S) less than $\pm 50\ \mu\text{Vdeg}^{-1}$, and Hall coefficients (R) which are not significantly different from R_0 , the free electron value. This type of liquid has been called a Type I alloy by Enderby and Collings [7] and includes a range of systems, e. g. (Bi-Te, Au-Te, Cd-Sb) which were once considered to be semiconducting in character (Joffe and Regel [8]).

There exists a second group of liquid alloys (Type II in the notation of Enderby and Collings) whose electronic properties are different from those of metallic (i. e. Faber-Ziman) systems and are rather similar to those of semiconductors. Such liquids are usually referred to as «liquid semiconductors». Two main types of liquid semiconductors have been identified, namely, those based on the chalcogenides (for example, liquid Cu_2Te) and those in which metals of vastly different electronegativities are alloyed together. These latter systems are of considerable interest because they enable the experimenter to follow continually the transition from metallic behaviour to semiconducting behaviour. Liquid Mg-Bi and Mg-Sb represent two of the alloys which are known to fall into this group. Experimental results for σ and S have been reported for liquid Mg-Bi by Ilschner and Wagner [9] and by Enderby and Collings [7]. At the composition Mg_3Bi_2 , the minimum value in σ is associated with a sign change in S and a positive $d\sigma/dT$. It is clear from this evidence and from the behaviour of the excess free energy that a major change in the bonding characteristics takes place as we proceed from pure liquid Bi or Mg to the liquid alloy Mg_3Bi_2 .

Some recent experiments on alkali metal based type II liquid alloys have been completed in our laboratory at Leicester. Results for S and σ for one of them (Li-Pb) due to Nguyen (private communication) are shown in figures 1 and 2. These results suggest that the dip in the conductivity coupled with a sign change in the thermopower is associated with a chemical valence effect and is not a direct consequence of the existence of a solid state compound. (There are four intermetallic compounds in the solid

Fig. 1. — The electrical conductivity of liquid Li-Pb
● 800°C ○ 850°C □ 900°C ■ 950°C.

Fig. 2. — The absolute thermoelectric power of liquid Li-Pb
● 800°C ○ 850°C □ 900°C ■ 950°C.

state but the anomaly occurs only at the composition Li_4Pb .)

Our basic understanding of these liquids is still in a very primitive state; the development of a comprehensive theoretical treatment in which the various electronic and thermodynamic properties of liquid semiconductors can be discussed, has been hampered by the lack of information about the nature of the atomic order which exists in alloys of this type. We therefore turn, in this introductory account of liquid metal physics, to problems associated with the structure of binary liquid alloys.

3. The structure of liquid alloys. — 3.1 PARTIAL STRUCTURE FACTORS. — We define a partial structure factor, $a_{\alpha\beta}$, through

$$a_{\alpha\beta}(q) = 1 + \frac{4\pi n}{q} \int dr [g_{\alpha\beta}(r) - 1] r \sin qr$$

where $g_{\alpha\beta}$ represents the distribution of type α -atoms observed from a β -atom at the origin, n is the number density of atoms irrespective of type, q is the conventional momentum transfer variable, and α and β are dummy suffices which take on the values 1 and 2 for a binary alloy. In terms of the differential scattering cross-section, a quantity which can be determined experimentally, it can be readily shown that

$$\frac{d\sigma}{d\Omega} = c_1 f_1^2 + c_2 f_2^2 + F(q).$$

Here c_1 and c_2 are the atomic concentration of two constituents, f_1 and f_2 the appropriate scattering factors and $F(q)$ is given by

$$F(q) = c_1^2 f_1^2 (a_{11} - 1) + c_2^2 f_2^2 (a_{22} - 1) + 2 c_1 c_2 f_1 f_2 (a_{12} - 1).$$

Thus, in order to discuss liquid alloys from a fundamental standpoint, three partial structure factors a_{11} , a_{12} and a_{22} are required. To obtain these, three separate determinations of $d\sigma/d\Omega$ for the same alloy must be made by changing f_1 or f_2 . It is now clear that the only feasible means of carrying out such experiments is to combine neutron diffraction methods with the use of isotopically enriched samples (Enderby, North and Egelstaff [10]).

As part of a continuing programme (see, for instance, Enderby *et al.* [10], Enderby and Howells [11]) designed to lead to a fuller understanding of the structure of liquid alloys, Hawker, Howe and Enderby [12] have recently completed measurements on liquid CuTe and liquid Cu_2Te . Three samples of CuTe and Cu_2Te were prepared using natural Te and (i) natural copper, (ii) copper enriched to 99 % with ^{63}Cu , (iii) copper enriched to 99 % with ^{65}Cu . The coherent scattering cross-sections for $^{\text{nat}}\text{Cu}$, ^{63}Cu , ^{65}Cu and Te are in the proportion 1 : 0.73 : 1.96 : 0.51.

Several conclusions have emerged from this study, the most significant being that the existence of clusters in semiconducting alloys of the Cu-Te type has not been confirmed. Such clusters were first postulated by Hodgkinson [13] and by Cohen and Sak [14] as a basis for a general discussion of the electrical properties of liquid semiconductors.

The partial structure factors for liquid Cu_2Te are displayed in figure 3, the vertical lines indicating the residual uncertainty due to the inevitable experimental errors in $F(q)$. Hawker *et al.* have drawn attention to three features which they consider to be worthy of special note :

a) the similarity between a_{CuCu} and the structure factor for pure liquid copper ;

FIG. 3. — The partial structure factors for liquid Cu_2Te at 1000°C .

b) the significant difference between a_{TeTe} and the structure factor for pure liquid Te ;

c) the absence of a definite feature in any of the partial structure factors corresponding to a « pre-peak » which was found in $F(q)$ at a q value of $1 \text{ \AA}^{-1}$.

The first feature suggests that the packing of the Cu ions in liquid Cu_2Te is a highly disordered one dominated by a hard-core interaction equal to that for Cu ions in pure liquid Cu, whilst the second one indicates that the covalent character of pure liquid Te disappears as Cu is added. These conclusions are consistent with the view expressed by Enderby and Hawker [15] that models involving Cu substitutions into covalent Te chains are unlikely to be useful as a starting point for explaining the properties of liquid Cu-Te alloys. The third feature illustrates very clearly the danger in attempting to relate maxima in $F(q)$, particularly at low q , to a particular distance in real space. The pre-peak in $F(q)$ simply reflects the effect of combining three partial structure factors each with a characteristic q -dependence. Hawker *et al.* found no evidence of long range order in any of partial radial distribution functions.

The extent to which the measured partial structure factors are consistent with a more or less random

FIG. 4. — $a_{11} - a_{22}$ as a function of composition

----- liquid Cu-Sn
 ----- liquid Mg-Bi
 (1/c₁ - 1/c₂).

mixture of Cu and Te ions in which substantial electron transfer has taken place is currently under theoretical

investigation by the Leicester Group. So far, this kind of model looks to be the most promising although considerably more numerical work will have to be undertaken before definitive conclusions can be reached.

3.2 THE LONG-WAVE LIMIT OF THE PARTIAL STRUCTURE FACTORS. — If we suppose that Type II alloys at the stoichiometric composition are essentially ionic in character, and that all the electrons are localized on ion sites, the Stillinger-Lovett [16] condition for electrical neutrality implies that

$$a_{11}(0) - a_{22}(0) = \frac{1}{c_1} - \frac{1}{c_2}.$$

Recently, the thermodynamic relationship for $a_{\alpha\beta}(0)$ derived by McAlister and Turner [17] have been applied to liquid Cu-Sn (a type I alloy) by Turner, Crozier and Cochran (*) and to liquid Mg-Bi (a type II alloy) by McAlister, Crozier and Cochran [18]. In figure 4 a comparison between $a_{11} - a_{22}$ and $\left(\frac{1}{c_1} - \frac{1}{c_2}\right)$ is made for both systems. The « ionic » curve fits the data only for the type II system in the region around Mg₃Bi₂ indicating that the electrical neutrality condition can be met over a range of composition almost entirely by considering the ionic structure factors alone. This strongly suggests that a gap (or pseudo gap) in the electron energy spectrum must have developed around the stoichiometric composition. A sufficient condition for

$$(a_{11} - a_{22}) = \left(\frac{1}{c_1} - \frac{1}{c_2}\right)$$

is that $\partial^2 G / \partial c_2^2 = \infty$ where G is the Gibbs free energy. Interestingly, Darken [19] has defined $\partial^2 G / \partial c_2^2$ as a « stability function » and finds that it exhibits large peaks at stoichiometric compositions which he empirically relates to valence considerations or the existence of solid state compounds.

(*) Private communication.

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