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PHOTOEMISSION FROM LIQUID Hg AND LIQUID Al

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Résumé. — On présente ici des mesures de spectres de photo-émission obtenues sur le mercure et l’aluminium liquides des énergies de photons allant jusqu’à 21.2 eV. Les résultats sont interprétés en densité d’états initiale et sont comparés avec les résultats du modèle d’électron presque libre pour les métaux liquides. Les lignes d’émission de cœur 5d du Hg sont clairement observées à —7.6 et —9.8 eV. En alliant avec l’indium les lignes se rétrécissent et s’éloignent du niveau de Fermi.

Abstract. — Photoemission measurements of liquid mercury and liquid Al are reported for photon energies up to 21.2 eV. The results are interpreted in terms of the initial density of states and are compared with the nearly free electron description of liquid metals. The 5d core emission lines of Hg are clearly revealed at —7.6 and —9.8 eV. On alloying with indium the lines narrow and shift away from the Fermi edge.

1. Introduction. — Theoretical descriptions of the electronic structure of liquid metals are made difficult by the need to average over all disordered configurations. Attempts to calculate the electron density of states have followed the perturbation treatment of Edwards (1962) and, with few exceptions, have suggested that the density of states curve differs little from a free-electron parabola. This approach is supported by many transport measurements which have been explained on the basis of the Ziman theory (Ziman, 1961). Studies of liquid simple metals using photoemission, an optical technique which probes electron states away from the Fermi level, have been reported by Koyama and Spicer (1971) for In, by Norris, Rodway and Williams (1973) for In and Sn and for low photon energies by Cotti et al. (1973) for Hg. These measurements question the weak scattering approach. We describe here photoemission measurements of liquid aluminium and liquid mercury which follow the same pattern as the earlier results.

In the following we assume the usual three step process (Berglund and Spicer, 1964) and since a liquid is a highly disordered system we also assume that conservation of the one-electron wave vector is not required during the optical excitation process. If as a further approximation the optical matrix elements are considered constant it follows that the energy distribution of photo-emitted electrons is related to the product of the initial and final densities of states. The total distribution \( N(E, \hbar \omega) \) for electron energy \( E \) and photon energy \( \hbar \omega \) is thus

\[
N(E, \hbar \omega) = B \rho(E - \hbar \omega) \rho(E) + \text{inelastically scattered electrons}
\]

The term \( B \) is a smooth energy dependent function and includes effects associated with scattering and escape. It is of note to point out here that contrary to the situation in a solid metal at room temperature the mean free path for electron ion scattering in a liquid metal is often shorter than the mean free path for electron-electron scattering. One consequence is that the effective probe depth will be shortened making the technique more surface sensitive.

2. Experimental. — The photoemission measurements were made under ultra-clean conditions using the same basic preparation and measurement technique as described before (Norris et al., loc. cit.). The sample containers, which were made of either molybdenum (Hg) or alumina (Al), were thoroughly outgassed before measurement. During the experiment the ambient vacuum was maintained at \( 2 \times 10^{-4} \text{ torr} \) (Hg) and \( 1 \times 10^{-9} \text{ torr} \) (Al), these values being governed by the vapour pressures of the liquid samples.

Exciting radiation was obtained using either a hydrogen discharge lamp coupled to a vacuum ultra violet monochromator with a LiF window \( (\hbar \omega < 11 \text{ eV}) \) or a windowless noble gas resonance lamp \( (\hbar \omega = 21.2 \text{ eV}) \).

3. Results. — 3.1 Hg. — Figure 1 shows three energy distribution curves (EDC’s) of electrons photoemitted from a freshly prepared Hg specimen using photon energies up to 10.2 eV. The results are normalized to the yield and for convenience are plotted against the energy of the initial state \( E_{\text{kin}} + \varphi - \hbar \omega \) where \( E_{\text{kin}} \) is the kinetic energy of the emitted electrons and \( \varphi \) the work function. Zero energy thus
corresponds to the Fermi level. The curves are characterized by a lack of structure immediately below the Fermi edge, in distinct contrast to the results for the tri and quadrivalent metals In, Sn (Norris et al., 1973) and Pb (Unpublished, 1973), a peak at \(-2.3\) eV and a hump of secondary electrons which moves progressively to lower energies with increasing photon energy. The persistence in the shape of the unscattered part of the curves supports the non-direct model and suggests in particular that the feature at \(-2.3\) eV corresponds to a similar feature in initial density of states.

Figure 2 shows the energy distribution curve obtained at 21.2 eV energy. The small feature at \(-2.3\) eV is again clearly visible. On alloying with indium this part of the curve changes as can be seen in the inset. A peak appears at the Fermi edge and the weak feature at \(-2.3\) eV is almost removed. The strong doublet at \(-7.6\) and \(-9.8\) eV is due to transitions from the occupied spin-orbit split 5d_{5/2} and 5d_{3/2} core levels.

The small hump at approximately \(-5.5\) eV is most likely due to transitions from the upper d level excited by the weak satellite \(\beta\) line which accompanies the main resonance line in a helium gas discharge.

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**Table I**

*Measured positions of the 5d_{5/2} and 5d_{3/2} levels in Hg and a Hg_{50}In_{50} alloy. Their widths are corrected for experimental broadening using a Gaussian of 0.5 eV half width.*

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Hg_{50}In_{50}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5d_{5/2}</td>
<td>5d_{3/2}</td>
</tr>
<tr>
<td>line energy eV</td>
<td>7.6</td>
<td>7.85</td>
</tr>
<tr>
<td>corr. width eV</td>
<td>1.0</td>
<td>0.75</td>
</tr>
</tbody>
</table>

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Figure 3 shows the energy distribution curve obtained with liquid aluminium, curve (c) immediately after pouring (a) and (b) after subsequent exposure to the ambient vacuum.
The energy distribution of electrons photoemitted from a freshly prepared sample of liquid aluminium at 700 °C is shown in Figure 3 (curve a). The curve which is corrected for thermal electrons reveals several features at 72.4, 2.5, 7.6, and 11.0 eV. Liquid aluminium is a particularly difficult material to measure due to its affinity for oxygen. Curves (b) and (c) were obtained from a liquid Al sample during the course of an experiment and clearly show that the peak at 6.5 eV is due to contamination. The other features are little affected and are, we suggest, characteristic of the pure specimen. Solid aluminium specimens were obtained by simply freezing the melt. The high energy part of an EDC obtained with solid Al is shown in Figure 4 and apart from the appearance of a small feature at 4.9 eV is broadly similar to the liquid curve. By using our preparation technique EDC's from solid Al could be obtained without the sharp edge at 10.2 eV interpreted as being due to a plasmon loss (Lindau et al., 1971).

4. Discussion. — The negative slope of the Hg EDC's at the high energy end contrasts with the theoretical calculations of Chan and Ballentine (1971) and of Ichikawa (1972) which suggest that the density of states is sharply rising at the Fermi level $E_F$. To explain other experimental properties Mott (1966) has proposed a strong dip in the density of states, the value at the Fermi level being 7 of the free electron value. We note that in the 21.2 eV curve where the effect of escape and secondary electrons is small the ratio of the height at the Fermi edge to that at 2.3 eV is 0.6. The behaviour on alloying is also not inconsistent with Mott's suggestion that the minimum in the density of states should weaken with increasing In content. The position of the weak feature in the mercury EDC's is close in energy to the point where the conduction band first touches the Brillouin zone in solid mercury as calculated by Dishman and Rayne (1968) (2.4 eV) and by Keeton and Loucks (1966) (2.7 eV). Although the agreement between the liquid and solid EDC's for aluminium is not perfect it can be seen from figure 4 that the feature at 2.5 eV persists in the liquid phase and is also coincident with a strong peak in the density of states curve for the solid, the liquid density of states curve being quite featureless. Such a correspondence between the liquid and solid EDC's and the solid density of states was also noted for Indium [Norris et al., loc. cit.] and would suggest that some aspects of the solid electronic structure persist on melting contrary to the predictions of the nearly-free-electron theory. Matrix elements may well be important and work is proceeding to incorporate them in a more complete analysis of the results presented here.

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References

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