PHOTOELECTRON SPECTROSCOPY OF LIQUID METALS

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INTRODUCTION:

The investigation of the electronic structure of liquid elements with photoelectron spectroscopy is restricted to some 20 elements of the periodic table. This restriction is mainly due to the high vapour pressures of most elements in the liquid state and the need of ultra high vacuum conditions in the spectrometer.

LIQUID METALS:

Despite the name they are not liquid, but solid at room temperature. Liquid metal alloys have number of desirable material features:

1) High tensile strength
2) Excellent resistance to corrosion
3) Very high coefficient of restitution (COR)
   (COR is a fraction of speed before and after impact)

TYPICAL APPLICATIONS OF LIQUID METALS:

These are used as Thermostats, switches, barometers, heat transfer system, heating designs and thermal cooling. These are generally stored in polyethylene bottles.

Photoelectron spectroscopy in liquid metals deals with the study of transition from solid to liquid state which can have substantial effect on the electronic properties of metals.

XPS STUDY OF LIQUID METALS:

ALKALI METALS (Li & Na):

The electronic structure of liquid alkali metals is of particular interest since these groups of metals represent the electronically simplest metals known in the periodic system. Particularly for Lithium finding an electronic structure close to the prediction of Free Electron Model (F.E.M). The spectroscopic studies of crystalline Li & Na gives some peaks with contamination where as in the study of liquid Li and Na have been prepared excellent stability against recontamination as checked both by UPS and XPS.

The valence band spectra of lithium are in agreement with a parabolic band whose width however proves to be significantly reduced compared to the FEM. In contrast the experimental band width of sodium exhibits a minor reduction from the FEM prediction whereas the valence band shape is rather triangular. Only minor changes of the relative 8 to p band state photo ionization cross sections as a function of the excitation energy have been observed within the range of hυ=11.8 - 48.4eV in contrast to the results on polyvalent metals. The use of He (II) radiation enabled a variety of observations.

A considerable number of studies have been performed for their solid phases whereas for the liquid state there exists only one experimental photoemission study so far and only a minor number of band structure calculations have been carried out. Generally the DOS calculations for Li and Na reveal a valence electronic structure close to the model of free or nearly free electrons for both the liquid and the solid phases. Excellent agreement of XPS valence bands with calculated spectra have been obtained for polycrystalline Na whereas deviations from the FEM, i.e. reduced band widths have been observed by photoemission studies of single crystalline Na. In this work we report the first photoemission results of liquid Li and Na obtained by using a wide range of excitation energies.

The valence band spectra of liquid lithium obtained with photon excitation energies ranging from 11.8 to 48.4eV in following Figure.

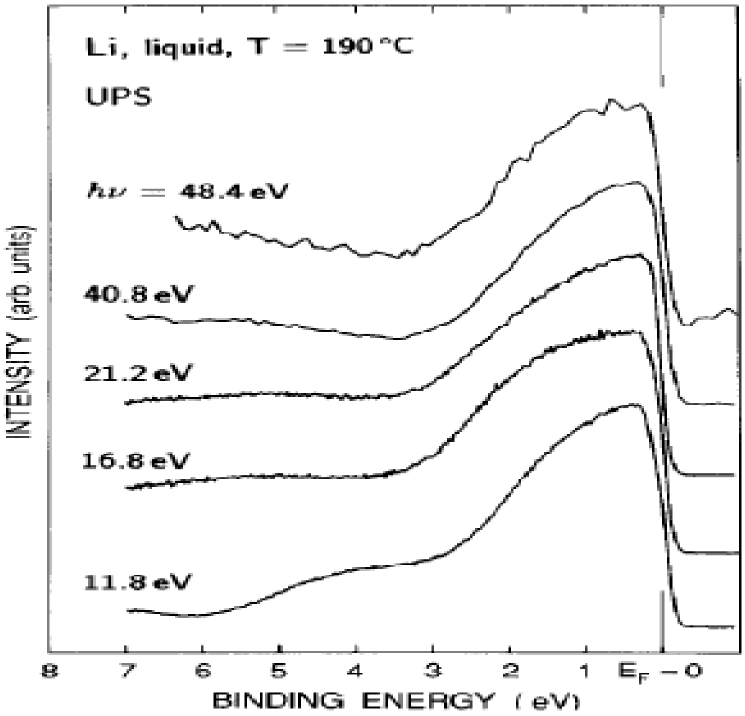

Figure:- UPS valence band spectra of liquid Li obtained with resonance lamp excitation: Ar (I) (hυ=ll.8eV), Ne(I)(16.8eV), He(I)(21.2eV), He(II)(40.8eV) and He(II)* (48.4eV)

At a first glance an overall similarity is observed, i.e. narrow valence band spectra of slightly rounded shape with maximum intensities near the Fermi level. Major differences can be seen in the change of the background. In fact the spectra obtained with hυ =11.8, 40.8 and 48.4eV turned out to be almost identical concerning their shape and their total bandwidth (~ 2.9eV). At medium photon energies however, a tiny but significant modification shows up in a more rounded shape and an enlarged width of ~ 3.2eV.

XPS and UPS valence band spectra of liquid Na are shown in figure below . Features similar to the case of liquid Li can be observed i.e. a narrow band with maximum intensity near EF. However all the spectra exhibit a triangular shape of the valence band and even less variations of the spectra are observed in the UPS regime, where the width of the Ar I spectrum is slightly diminished. The XPS spectrum however reveals a significant increase in band width leaving the overall shape triangular.

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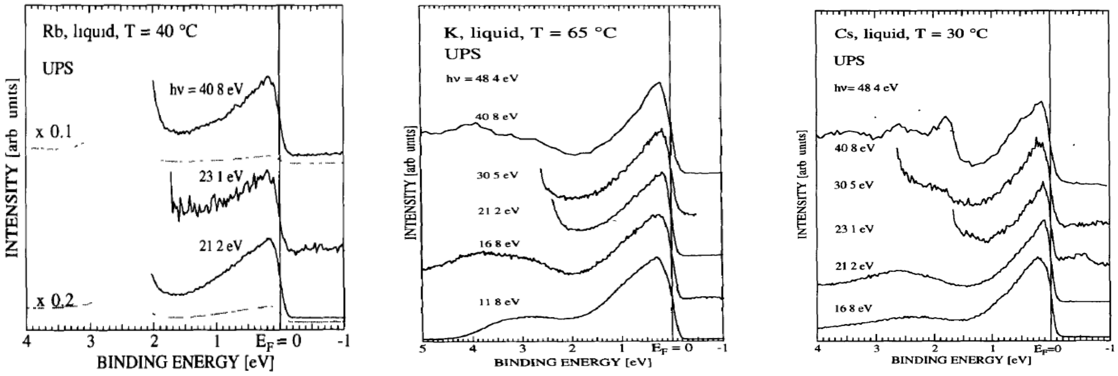

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Figure:-TR-PES valence band spectra of Pd during laser pulse heating with pulse energy of 0.33J/pulse and a base temperature of 780K.

The figure showed above is the UPS valence band structure of Pd measured in eight different time windows with defined starting times with respect to the laser pulse. Time windows W1-W7 cover a time length of 14 microseconds having duration of 2 micro second each. W1 starts 2.3microsecs before the onset of laser pulse and W8 starts 5 ms after the onset of the laser pulse for duration of 2ms. The W1 and W8 time windows, therefore, measure the spectra of at the base temperature, which is 780 K in case of Pd. The melting point of Pd is 1828 K and it is heated 100 K above this temperature to measure the W2 spectra. The W3 spectra correspond to the highest sample temperature when the sample is only in the liquid state.

The shape of the spectra changes remarkably at the phase transition. There is a shift of the maximum intensity from 2eV to 0.8eV and formation of a weak shoulder near 2.5eV. The spectra measured in time windows W4-W7 reveal a gradual change towards the spectrum obtained at the base temperature associated with gradual cooling of the sample surface.

Similar experiments have been performed on a Molybdenum (110), Niobium (110) and Tungsten (111) single crystal.

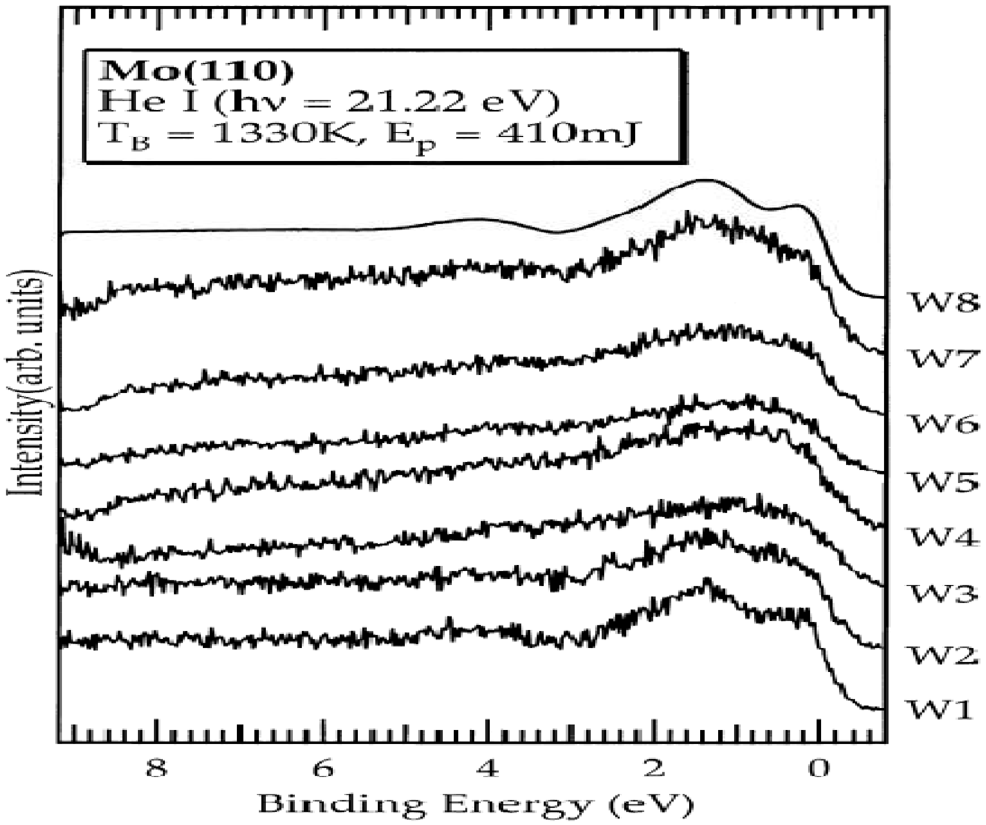

Figure:- He(I)-UPS valence band spectra of Mo during melting by a laser-pulse with energy 410mJ, corresponding to an energy density of 23 J/cm^3. The base temperature TB is 1330 K. The first seven spectra W1±W7 have duration of 2 μs each and were taken subsequently. W1 starts 1.9 μs before the laser pulse. W8 has duration of 2 ms and begins 5 ms after the laser pulse. Resolution of the spectrometer is 84meV.

Photoemission results are summarized in above figure. Here, spectra W1 and W8 are from a clean Mo surface at 1330 K. Three intensity maxima are visible at the binding energies of 4.2, 1.5 and 0.3eV. As in the case of Pd, changes are induced in the photoelectron spectra upon the phase transition, leaving only one peak in the liquid phase (W3). In this case, the analysis of the Fermi edge broadening yields a temperature of T = 3030±100 K, which is close to the melting temperature of Mo (2890K). During cooling (W4±W7), the spectra continuously approach the shape of the solid reference (W8).

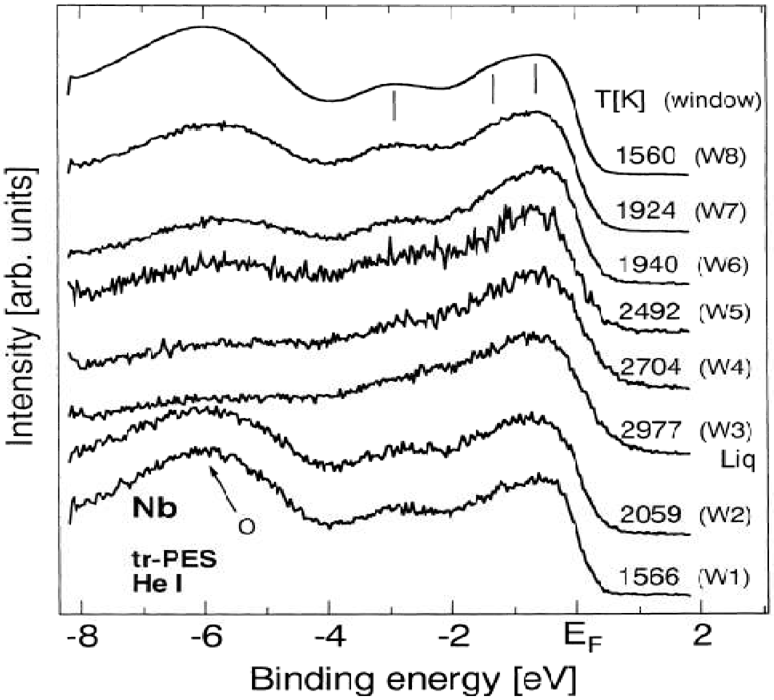

Figure:-Time-resolved spectra of niobium normalized to the same height at 0.6eV binding energy. The vertical ticks on time window 8 spectrum show the observed structures. The label 'O' shows an oxygen contamination peak.

The samples were polycrystalline foils with a thickness between 0.7 and 1 mm. They were pre cleaned with sandpaper and acetone / ethanol before being cleaned in situ by several heating and sputtering cycles. The cleanliness of the samples was determined by monochromatized XPS (MXPS) measurements. In a few cases it was not possible to obtain atomically clean surfaces (see below) due to the diffusion of contaminants (usually sulfur and/or oxygen) from the bulk to the surface at elevated temperature.

In the above figure spectra are normalized to the same height at 0.6eV binding energy. The changes of the spectral shape between solid and liquid state can be seen by comparing time windows 1 or 8 (both in the solid state) to time window 3 (liquid state). The main change between liquid and solid phase spectra is a smoothening of the structures in the liquid phase. The three structures encountered in the solid state spectra (see window 8) are reproduced, though less pronounced in the liquid state spectra. The peak at -6eV is an oxygen contamination peak (as indicated in above figure) which disappears in the liquid state and whose increase in the time windows 4–8 shows the diffusion from the bulk.

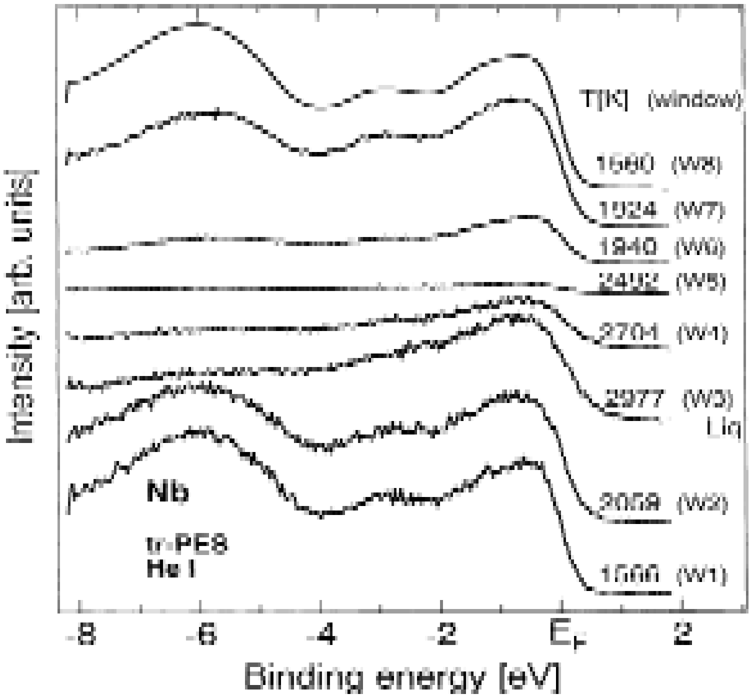

Figure:-The figure shows same spectra as in but now normalized to the same acquisition time. A decrease in intensity is clearly visible for time windows 4–6.

The desorption of oxygen has also been seen by TR-MXPS measurements of the O1s peak. The poorer statistics of the windows 5 and 6 is due to their low count rate. It appears more clearly on above figure where the same spectra normalized to the acquisition time are shown. This dramatic decrease in intensity is due to thermal emitted electrons (thermionic emission), which form a space charge above the sample and act as a dispersion lens for the photo emitted electrons. This space charge influences the photoelectron count rate only since the kinetic energy is conserved after passing completely the electron cloud.

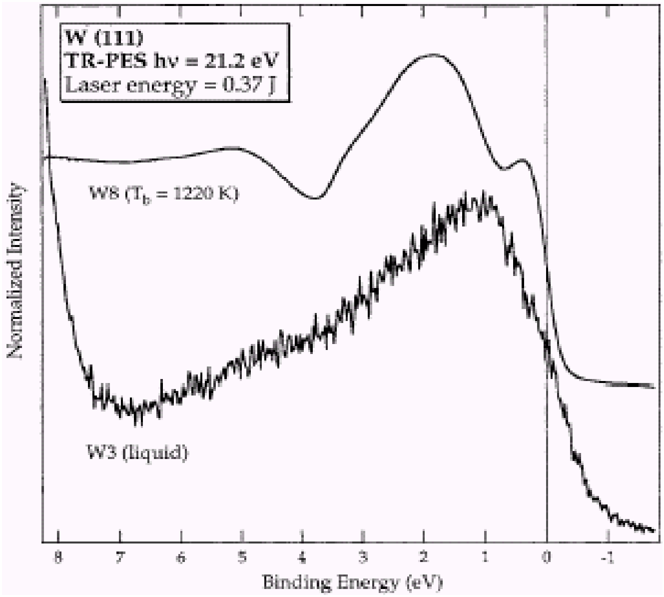

Figure:-TR-PES valence band spectra of W: the liquid phase measured at 3700 K and the solid phase measured at the base temperature of 1200 K.

Given above figure the valence band spectra of W. Here also as in the case of Mo, a complete change of spectra is observed at the phase transition. The two peaks at 0.4eV and 1.8eV in the solid phase form one common band in the liquid phase and the peak at 5eV is not clearly visible in the liquid phase.

The experimental results that were observed on melting were only minor changes in the valence band for Group V metals Nb and Ta, distinct change of the valence band of Pd at the phase transition and marked changes in valence band spectra of Group VI metals Mo and W.

X-RAY ELECTRONIC MAGNETIC SPECTROMETER:

The valence band photoemission spectra of Ni and Cu metals in solid and liquid states are measured using a magnetic
Spectrometer. The valence band width is narrower in the liquid state than in the solid state. The difference in the fine structure of the valence band XPS- spectra of transition metals between liquid and crystalline state can be explained: first, by the change of the local order, the chemical bonding, and the delocalization of d-electrons during the disordering process; and, second, by the enhancement of overlap of the d-electron orbital of nearest neighbor atoms in clusters of the liquid compared to the crystalline metal.

The XPS-spectra of valence bands and core levels e obtained by the X-ray electronic magnetic spectrometer, which allows us to investigate the samples in other the solid and liquid states in the temperature range 293-1800 K. To obtain a clean surface on the samples, mechanical cleaning 'in situ' is carried out with a tungsten brush and the cleanliness of the surface is checked by measurement of the XPS- spectra of Cu3p, Ni3p C Is and O 1s core levels. The samples are heated in the main chamber of the spectrometer by a resistive stove with a bifilar heating coil up to the required temperature, which exceeds the melting point by 100 K. This temperature is maintained for 1 h.

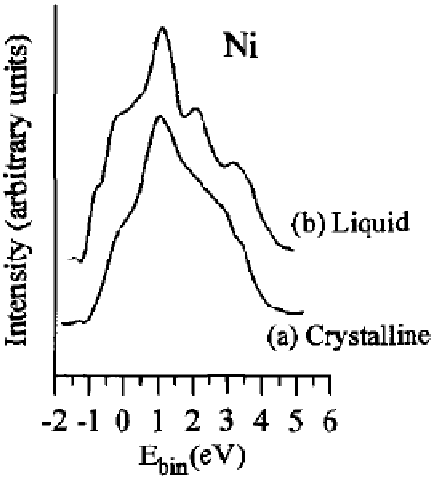

Figure:-The XPS spectra of the valence band of Ni: (a) crystalline state at room temperature; (b) liquid state at 1850 K.

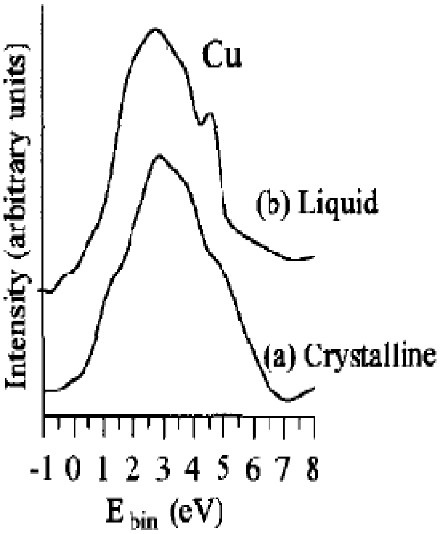

Figure:-The XPS spectra of the valence band of Cu: (a) crystalline state at room temperature; (b) liquid state at 1700 K.

The XPS-Spectra comparison is made for the XPS-spectra of valence bands of the metals Cu and Ni in the solid and liquid states. The exciting source is the A1Kc~-radiation (hʋ=1486.6eV) line. The valence bands XPS-spectra are known to reflect the distribution of the density of states (DOS) of d-electrons in transitional metals. This is due to the higher ionization cross-section of the d-electrons compared to the s- and p-electrons. Comparing the curves in Figs. 1 and 2, one can see that in the liquid state the fine structure in the spectra is displayed more clearly and the valence band width is narrower than in the solid state. Narrower features are specific to the spectra of isolated atoms.

The shape of the Cu3s core level spectrum differs in the liquid state from that in the solid state of Cu metal. It is well known that the core level XPS-spectra of transition metals have a complicated shape due to the multiple splitting effects. The electrostatic interaction between the unfilled 3d-shell and the ionized shell of a transition metal atom results in the multiple splitting of the XPS core line. Therefore, several lines due to the different final states are observed, the intensity and the energy of which is determined by the number of unpaired 3d-electrons.

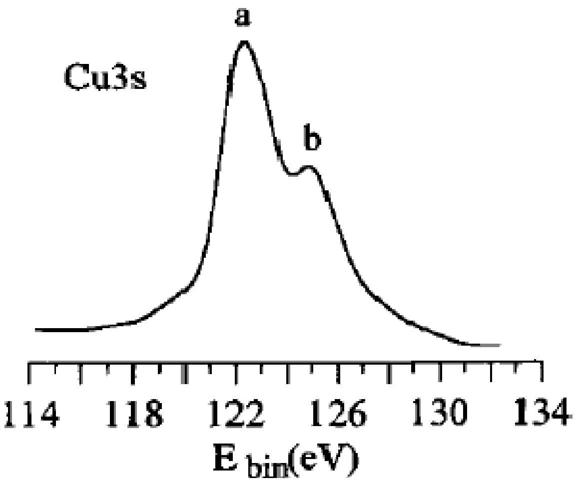

Figure:-Cu3s XPS spectrum of the liquid Cu at 1700 K: (a) main maximum; (b) maximum due to the multiple splitting effects.

In the above XPS-spectrum of Cu 3s spectrum, two final states are possible. In the Cu3s- spectrum obtained from the crystalline Cu, the multiple splitting is absent. In contrast, in the liquid Cu, two lines separated by 2.35 eV appear (Fig. 3). The intensity ratio of the a-maximum to the b-maximum is 1.8. This suggests the appearance of unpaired 3d-electrons, which is possible if the 3d-electrons are involved in covalent bonding with the electrons of neighboring atoms. Thus, the investigations of the Cu3s core level spectra of transition metals confirm the fact that there is enhanced overlap of the d-electron orbitals of the nearest neighbour atoms in clusters of the liquid Cu.

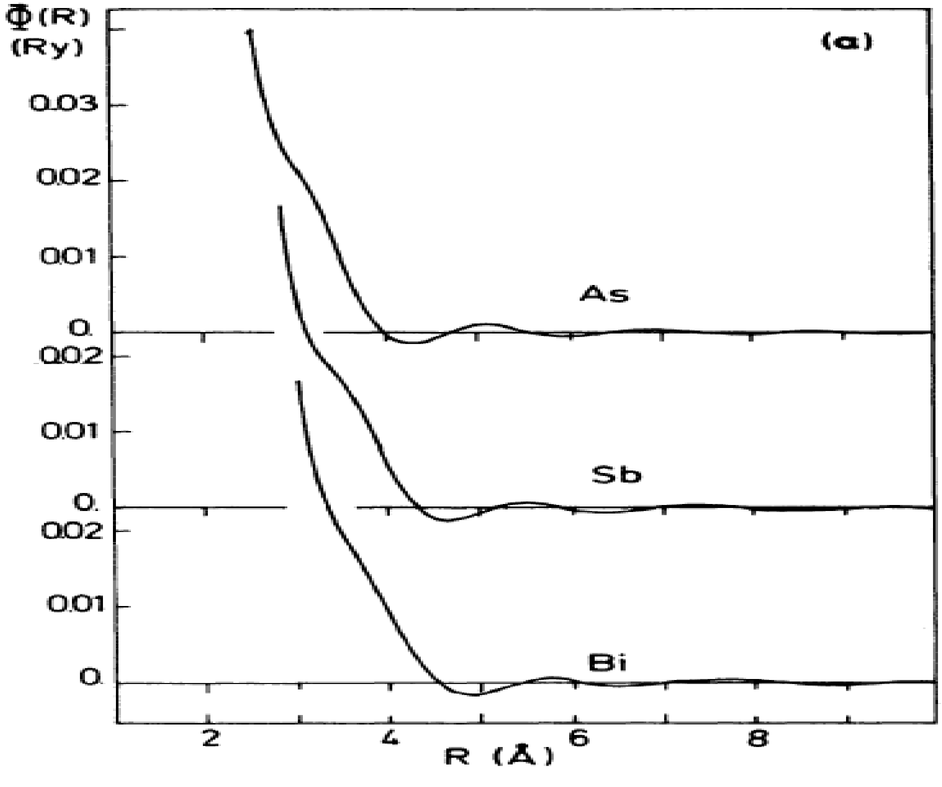

Figure:-Effective pair interactions Ø(R) in liquid As, Sb and Bi, calculated using the optimized orthogonalized plane-wave pseudo potentials and a full relativistic treatment of the core states.

References:

1. I.N. Shabanova, A.V. Kholzakov, V.S. Kraposhin, Journal of Electron Spectroscopy and Releted Phenomena, 88-91, 453-455 (1998).
2. R. Wahrenberg, M.G. Garnier, H. Stupp, P. Oelhafen, Journal of Electron Spectroscopy and Releted Phenomena, 114-116, 1083-1087 (2001).
3. F. Baumberger, W. be, T. Greber, J. Osterwalder, Science, 306, 2221(2004).
4. H. Stupp, H.G. Boyen, G. Gantnery, P.Oelhafen, J. Phy. Condens. Matter, 8, 9373-937 (1996).
5. J. Hafner, W. Jank, Physical review B, 45, 2739-2749 (1992).
6. Akito Kakizaki, Michio Niwano, Hiroshi Yamakawa, Kazuo Soda, Takehiko Ishi and Shoji Suzuki, Journal of Non-Crystalline Solids, 117-118, 417-420 (1990).
7. Tery L. Barr, Applications of Surface Science, 15, 1-35 (1983).