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Abstract

The $L_{2,3}$ excitation spectra in liquid Na and Al and in solid samples at several temperatures were measured with yield spectroscopy. The spike at the Na edge at about 31 eV is observed virtually unchanged in the liquid. This is in support of a many body interpretation. The broader structures up to 100 eV above the edges in Na and Al are washed out in the liquid. This is in qualitative agreement with an EXAFS interpretation.

Recently considerable theoretical effort is being made for interpreting the 2p core electron transitions in simple metals. One-electron and many-electron theories are competing for an explanation of the structures at the onset of transitions and in the region up to more than 100 eV above threshold. The spike at the Na $L_{2,3}$ edges seemed to be well explained as a many-body effect by Mahan[1] and by Noziéres, de Dominicis and co-workers[2] as being a consequence of the shielding of the localized core hole by the metal electrons. The same theory predicts the rounding of K edges and conspicuous changes of edge shapes upon momentum transfer[3] (x-ray Raman scattering, electron energy loss scattering). Dow and co-workers[4] have disagreed especially with the many-body explanation of the rounding of the Li K edge and have proposed that a thermal broadening mechanism prevails. We could recently verify thermal broadening experimentally.[5] Also electron energy loss scattering experiments by Ritsko et al.[6] did not produce the predicted changes. From this and other facts[7] questions arise with respect to the limitations of the many-body theory.[1,2] The spike at the Na edge still provides an outstanding experimental support of this theory. Unlike similar, though weaker, features at the $L_{2,3}$ edges of Mg and Al the spike in Na cannot be pushed aside as being a density of states structure. Its behavior upon melting, nevertheless, should give an important clue for or against any many-body interpretation.

A thorough theoretical treatment of the free electron gas in the presence of a core hole produced still other collective resonances[8,9] which can be visualized as localized plasma oscillations the so called plasmarons. The first calculation[8] was in good agreement with the prominent peak at 24 eV and two shoulders at 15 eV and 30 eV above the onset of transitions in the $L_{2,3}$ absorption spectrum of Al. Similar structures in the $L_{2,3}$ spectra of Na and Mg did not show the proper scaling with the free electron density. It was demonstrated that these structures are absent in the spectrum of Na vapour[10] and Al vapour,[11] which proves that they are not of atomic origin. These experiments did not, however, exclude collective oscillations. Recently Ritsko et al.[12] have interpreted this structure as extended absorption fine structure (EXAFS). This is scattering of the outgoing electron wave function from the neighboring atoms back to the excited atom. Positive or negative interference modulates the matrix element, thus generating the minima and maxima as a function of the electron wavelength.[13,14] This is an effect strongly dependent on cristalline order. Ritsko et al.[12] reproduced part of the structure by a crude model calculation. Again, the behavior of this structure upon melting should discriminate between plasmarons and EXAFS.

The results were obtained by measuring the partial photoelectric yield which is known[15] to be proportional to the absorption coefficient. An electron energy analyzer[16] served to isolate scattered electrons from thermally emitted electrons. The light source was monochromatized[17] synchrotron radiation from DESY with a resolution ~ 0.15 eV at 50 eV photon energy. The samples were cleaned and maintained in a vacuum in the 10^{-10} Torr range. Care was taken to keep the initial oxide layer on the Na samples thin. It was removed after melting by stirring and scraping with a brush made out of tungsten wires. Clean Na, once obtained, could be maintained for many hours in the liquid state and for about one hour in the solid state without indications of oxidation. Na could be investigated between LNT and 390K (MP 371K). Al had to be supported on Al_2O_3 ceramics because it readily alloys with all metals. Measurements could be performed only between about 500 K and 1000 K (MP 933 K) since the ceramics was insulating at lower temperatures and the sample would charge. Only the temperature of the Na sample could be measured with a thermocouple.

Since an energy dependent though smooth factor[15] is connecting yield and absorption coefficient and since in addition the photon intensity could not be measured direclty we have corrected the yield spectra by multiplying with a smooth structureless empirical function. This function was determined in such a way as to bring the measured 'yield' of solid Na (LNT) into coincidence with the known absorption coefficient of Na (LNT),[18] which both showed virtually the same structures but a different general shape. The yield curves of the liquid metals therefore reflect the directly not accessible absorption coefficient.

Fig.1 shows the results on Na. The relative scales for solid and liquid Na are arbitrary. If the curves are scaled to bring them into coincidence near the onset of the $L_{2,3}$ transitions, the spike at the edge is virtually unchanged within the experimental accuracy, which is about 10% for the partial yield of the liquid below 35 eV (low photon intensity) and about 3% elsewhere. A slight broadening of the initial rise at the edge is observed and only an indication of the spin-orbit splitting is seen while it is well observed in the LNT absorption measurements.[19] The reduced accuracy of the partial yield measurement precludes a quantitative analysis of these small changes. The virtually unchanged presence of the spike in liquid Na excludes any explanation as an effect generated by crystalline order. This is a strong indication for an interpretation which involves the core hole in contact with a free electron gas as given by the presently available many-body theories.[1]

We now turn to the spectra at energies above the edges. In this region there is a striking difference between the spectra of liquid and solid Na. Obviously the structures E and F are washed out in the liquid and the shape of the liquid spectrum is quite similar to the free atom calculation by McGuire.[20] These calculations have also given the general shape of the spectrum of Na vapor.[10] Structures C and D are also absent in the liquid. In the solid they might be density of states peaks or peaks originating from traces of oxide. When samples are warmed up from LNT to RT a continuous change of structure in the energy region between E and F is observed. The minimum becomes weaker and flattens out.

Fig.2 shows the absorption coefficient of Al at RT and the yield spectrum of hot and liquid Al. The liquid Al spectrum shows the same wash-out of structure as the liquid Na spectrum does. The structures in the yield spectrum of hot solid Al (after cooling down for one hour after solidification) are less pronounced as in the absorption measurement made with samples at RT.[18] A measurement just after solidification of the sample showed even weaker structures.

It is clear that there is considerable change in structures for both Na and Al depending on temperature as well as on the state of the metal. This cannot be explained by the plasmaron theory[8,9] or any other many-body theory involving the free electron gas of a metal. The observed changes can be explained qualitatively using the EXAFS theory.[13,14] Rising temperature washes out the radial distribution function which determines the EXAFS structures.[13] Upon melting the long range order in the sample is destroyed and most of the structurs disappear. Part of the structures, however, is still present because the next nearest neighbor correlation is maintained in the liquid.

We have tried a model calculation for the interpretation of preliminary results[16] on Al using simple scattering theory with square well potentials quite similar to the calculation by Ritsko et al.[12] Ashley and Doniach,[14] however, are showing that EXAFS in the region of low kinetic energy of the emitted electrons is predominantly an effect of multiple scattering of the outgoing electron wave function from the first and second coordination shell with respect to the absorbing atom. For a quantitative calculation of structure in this low energy regime such an improved EXAFS theory, possibly including initial and final state symmetry[21], or a method matching atomic with solid state wave function at the edge of the atom as proposed by Fano[22] is obviously required.

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Figure Captions

Fig. 1: Photoabsorption[18,19] and photoyield of solid and liquid Na in the region of $L_{2,3}$ absorption. Absorption and yield of solid Na was obtained at LNT (same curve, see text). The liquid (yield) was measured at 390 K. Included are results of an atomic calculation by McGuire[20].

Fig. 2: Photoabsorption[18] and photoyield of solid and liquid Al in the region of $L_{2,3}$ absorption. Absorption of solid Al was obtained at RT and yield at about 500 K ('solid hot'). The liquid (yield) was measured at about 1000 K. Included are results of an atomic calculation by McGuire[20].

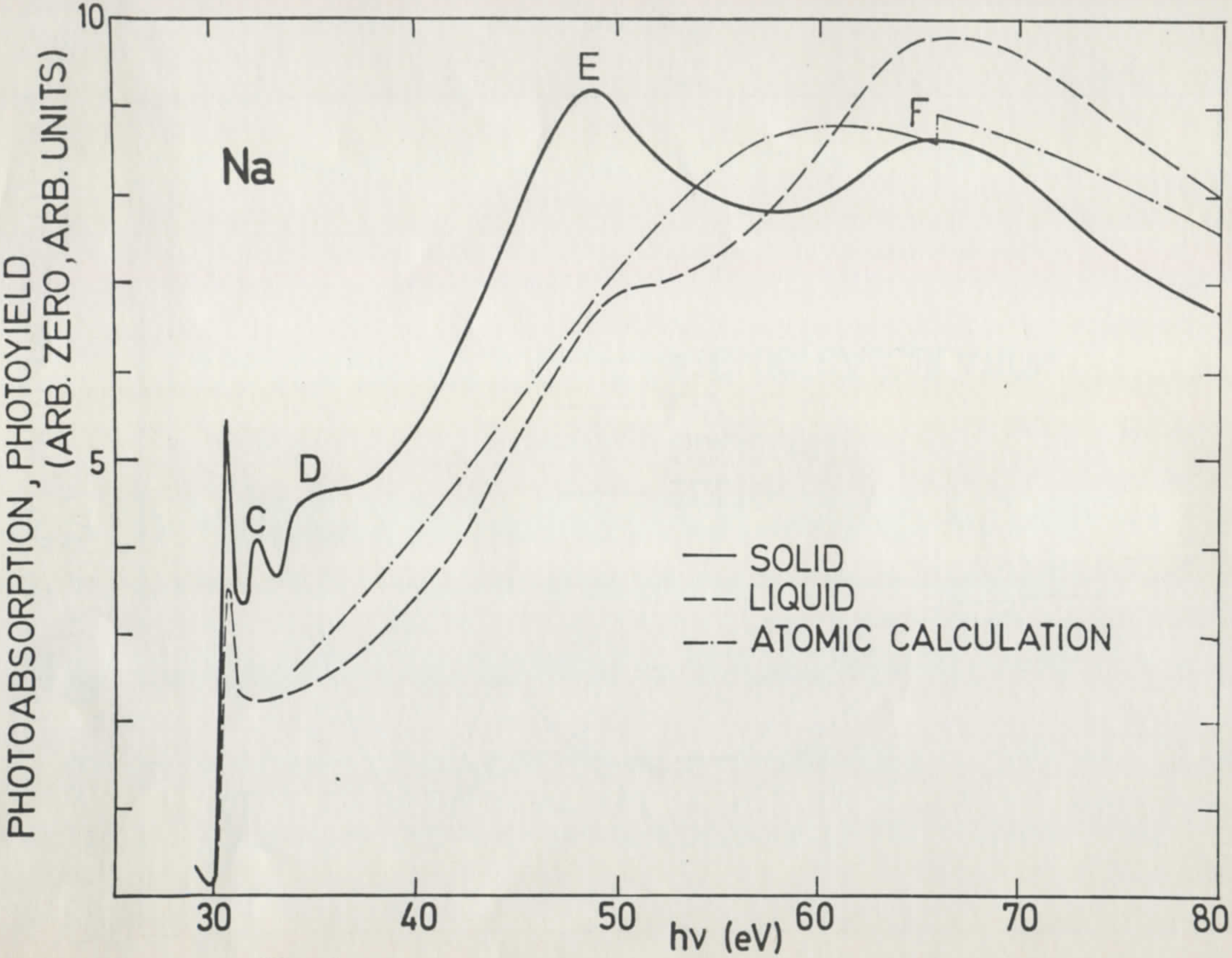
10
5
PHOTOABSORPTION, PHOTOYIELD
(ARB. ZERO, ARB. UNITS)
Na
C
D
E
F
SOLID
LIQUID
ATOMIC CALCULATION
30
40
50
60
70
80
hv (eV)

Fig. 1

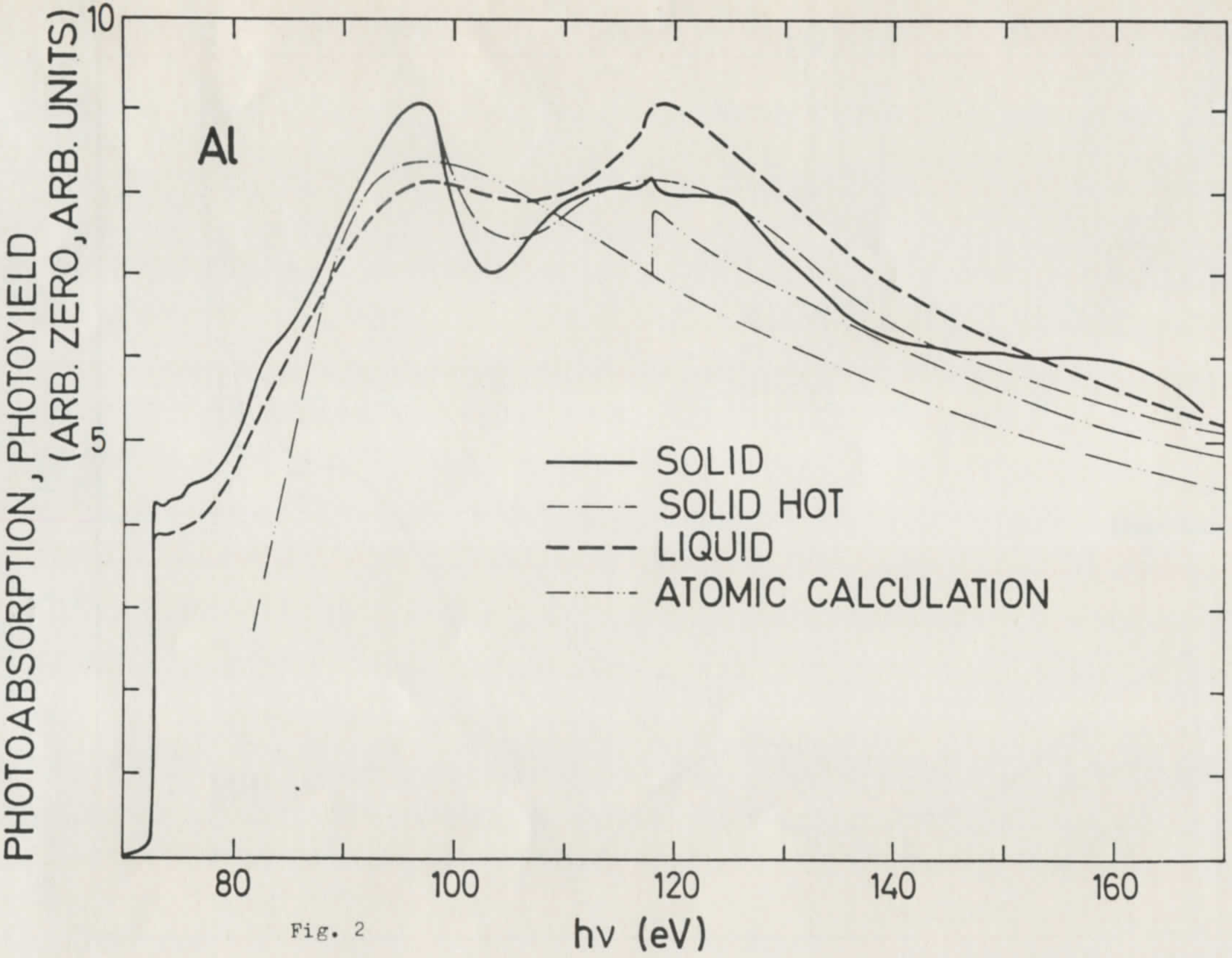
Al
PHOTOABSORPTION, PHOTOYIELD
(ARB. ZERO, ARB. UNITS)
10
5
80
100
120
140
160
hν (eV)
SOLID
SOLID HOT
LIQUID
ATOMIC CALCULATION

Fig. 2