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Density of States in the K Excitation Spectra of Solid and Liquid Lithium

by

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Density of States in the K Excitation Spectra of Solid and Liquid Lithium

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Photoelectric yield measurements at the Li K edge and in an extended energy range 54 - 80 eV are presented. The sample temperature was varied in the range 79 - 480 K (the liquid state). The edge consists of a steeply rising part due to the onset of transitions and a more slowly rising part which is interpreted as a rising density of states at the Fermi energy. With rising temperature the edge shifts to higher energy and broadens. Phonon broadening appears to contribute also at 79 K to the width while the edge shape is consistent with a threshold exponent $\alpha_1 \gtrsim 0$. *The structures in the range 54 - 80 eV are washed out on melting. These structures are well described by APW-calculations by Bross of the optical density including plasmon damping.*

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Introduction

It is well known, that the soft x-ray absorption cross section of simple metals like Na and Al follow the cross section of the respective atoms with a discontinuous edge at the onset (Wolff et al. 1972, Bruhn et al. 1976). Only an at most 10 % modulation, which can be explained within the EXAFS-model is superimposed onto this shape (Ritsko et al. 1974a, Petersen and Kunz 1975). As demonstrated in Fig. 1, with Li the situation is quite different: There is a strong deviation from the well known saw-tooth profile, which is observed in K-shell absorption spectra of heavier elements and which represents the atomic cross section.

Another important anomaly of the Li K spectrum occurs directly at threshold: The K-edge as measured in absorption spectra - included in an enlarged scale in Fig. 1 - is very broad. This broad threshold of the lightest metal which has its counterpart in fluorescence emission spectra has been a puzzle for decades (Skinner and Johnston 1937) and was extensively investigated both theoretically (e.g. Nozieres and deDominicies 1969, Mahan 1967,1974, McAlister 1969, Dow et al. 1973, Ritsko et al. 1974b) and experimentally. In 1974 we showed, that the width of the edge is strongly temperature dependent (Kunz et al. 1974) and in 1975 we were able to demonstrate, that a rising optical density of states (ODOS) is the dominating rounding mechanism at threshold (Petersen 1975a),

In this paper we report recent photoyield data which cover the energy range 54 - 80 eV. Our sample temperature was varied between 79 K and 480 K. Since the photoyield is proportional to the absorption coefficient in the vacuum-ultraviolet (e.g. Gudat and Kunz 1972) we were able to determine the absorption cross section of the liquid state of Li (melting point 452 K). We discuss these data under consideration of several band structure calculations (McAlister 1969, Shaw and Smith 1969, Bross 1973), part of which account for electron-electron correlations and extend to energies more than a Rydberg above the Fermi level. Moreover the experimental situation concerning the K-edge is briefly reviewed and we try to give a consistent picture which accounts for broadening mechanisms like core-hole phonon coupling, Auger lifetime broadening, the Mahan-Nozieres-deDominicis final state interaction and influence of the optical density of states directly above threshold.

Experimental procedure

The spectrally continuous radiation from the Deutsches Elektronen-Synchrotron DESY and a special monochromator with a fixed exit beam (Dietrich and Kunz 1972) served as a light source. The photoemission was measured under ultra high vacuum conditions ($\sim 2 \cdot 10^{-10}$ Torr) using an electrostatic energy analyzer and a channeltron multiplier. This technique offered the opportunity to measure both electron energy distribution curves (fixed photon energy, kinetic energy of electrons scanned) and photoyield spectra (fixed electron energy, photon energy scanned).

The yield spectra discussed here were recorded with a low resolution of the electron energy analyzer, typical values were ΔE = 2 eV, transmission energy 100 eV. This improved the counting rate of the inelastically scattered electrons, which were taken as representative for the yield (partial yield method). The resolution of the electron analyzer does not influence the spectra since

only the resolution of the monochromator ($\Delta E \approx E_{phot.}/500$) is relevant in this type of measurement. Unlike with Al (Petersen and Kunz 1975) the peak of directly excited electrons into the analyzers energy window could not be observed and spectra obtained as different kinetic energies were selected had the same shape. Our statistical error is about ±2 % in the partial yield mode. In another experimental arrangement using the total yield method - no energy analysis, open electron multiplier - we reduced this to less than 1 % to obtain high precision measurements directly at threshold.

Li was investigated on a directly heated Ta-strip. A stainless steel protected thermocouple and a tube of 2 mm diameter for liquid nitrogen were molten into the sample under Ar gas protection. Thus a good metallic contact between the sample and these components was obtained, liquid nitrogen cooling led to a measured temperature of 79 K. During the bake-out process the sample was cooled by running water through the tube. After bake-out when the pressure was in the 10^{-10} Torr range, the samples were cleaned: The oxide layer was scraped away with a tungsten-brush, the sample was then liquefied and remaining oxide particles were removed. Oxidation was monitored by measuring the ratio of the edge discontinuity with respect to the signal below the edge. The ratio 6:1 was our largest value, it decreases with oxidation because of the high absorption cross section of oxygen at 55 eV photon energy (Lee et al. 1973). Calculations of the valence band absorption cross section at 55 eV (McAlister 1969) indicate that with the optimum ratio 6:1 oxide on the sample indeed is negligible.

Experimental results and discussions

Figure 2 shows the region near the K-absorption threshold with its obvious deviation from the saw-tooth like atomic cross section, which sets in at the ionization threshold of the free atom at 60.6 eV (McGuire 1970, Ederer et al. 1970). This deviation is observed in both the solid and the liquid state, it is

obviously less pronounced in the latter. The curves labeled "ODOS" are APW-calculations of the optical density of states for K-absorption (Bross 1973). Both the one-electron-approximation and a curve which accounts for electron-electron correlations are shown. When the influence of collective oscillations of the electron gas is included (plasmon damping), the peak N_3^1 decreases (Bross 1973). This leads to an improved agreement with experiment. Note the one-to-one correlation between structure in the experimental curve on solid Li and the theoretical curve. To our knowledge, calculations of the density of states (DOS) for the liquid phase of Li are only available for energies near the edge, such a calculation is shown in Fig. 3.

This figure shows the threshold region for solid and liquid Li in an enlarged scale. Included is a model potential calculation of the DOS (Shaw and Smith 1969) and a calculation of the ODOS (McAlister 1969). The DOS includes eigenstates of all symmetries and matrix element effects are not accounted for. However, near the extrema at the Brillouin zone boundary the states are purely p-symmetric and a strong variation of the matrix element within an energy interval of about 2 eV does not occur (McAlister 1969). This justifies a comparison with the absorption spectra from the s-like initial state; around the Fermi level the projection of the p-symmetric part of the DOS should decrease like the ODOS. There is good agreement between theory and experiment for both the solid state and the liquid state spectra. As pointed out by one of us in a previous paper (Petersen 1975a), the threshold shape at 79 K is clearly determined by a rising ODOS. This effect is less dramatic in the liquid.

Going from the solid to the liquid there is obviously a considerable broadening of the threshold and an increase in the excitation energy from the core to the Fermi level. As mentioned above, this temperature broadening was first observed by Kunz, Petersen and Lynch in 1974. At that time, however, an influence of the

ODOS had not been experimentally verified. Consequently we interpreted our data under the assumption of a flat, free-electron like ODOS at threshold. The 10 % - 90 % values given by Kunz et al. 1974 are therefore too large and, as mentioned in the paper which pointed out the ODOS effect (Petersen 1975), we have to reinterpret the spectra near threshold at various temperatures under consideration of the rising ODOS.

Figure 4 shows a remeasurement of the spectra at different temperatures. The agreement with the result of Kunz et al. 1974 with the exception of the kink in the 79 K curve is good, the shifts relative to each other are more reliable now since the same monochromator was used for the whole set of data. Kunz et al. 1974 attached the 100 % - value of the edge for all temperatures to the peak at 55.5 eV photon energy, which is now identified as a maximum in the ODOS. The DOS effects at threshold suggest a relative scaling as given in Fig. 4. We are guided by an observed continuous wash out of the minimum at 57 eV photon energy with rising temperature. This scaling is used consistently in all the Figs. 2-4.

The analysis of the 10 % - 90 % values of the edge at 79 K is not a trivial problem since five threshold broadening mechanisms are involved: 1) the rising ODOS, 2) temperature broadening of the Fermi level, 3) Auger lifetime broadening, 4) broadening due to core hole - phonon coupling, 5) instrumental resolution. Moreover, threshold rounding caused by the MND-final state interaction was often claimed to be important (e.g. Mahan 1974). For Li there appears to be no experimental evidence in support of such a claim (Ritsko et al. 1974, Petersen 1975, Baer et al. 1976).

The 10 % - 90 % value of the 79 K edge is estimated by eye-ball inspection of this curve, which is the only one that shows a kink indicating the onset of the region, where the rise is determined by the ODOS. The 10 % - 90 % values

of the higher temperature curves are determined by positioning the 10 % and 90 % values at the same levels. 10 % and 90 % levels given in quotation marks are deduced from a fit by Baer et al. 1976 to the 79 K curve as given by Petersen 1975 with larger statistics. These authors convoluted data similar to those which they obtained from an XPS line shape analysis (sample temperature 90 K) with the rising ODOS and found consistency between both experiments. The numerical values of the widths are given in Table I together with our old 10 % - 90 % values of the total width of the whole rising part up to the peak.

Obviously there is a strong phonon broadening of the edge at higher temperatures. The phonon induced width of the 79 K - curve is difficult to determine because of its sensitivity to the Auger lifetime width, which was given by Baer et al. as 40 ± 20 meV.

Recently Callcott and Arakawa (1977) have shown evidence for a complementary edge behaviour in the fluorescence emission spectra. They observe a steeply falling edge at 85 K, which at its steepest part coincides within 70 meV (this means within the experimental error) with our absorption edge at 77 K. At temperatures up to 490K a continuously increasing width of the emission edge is observed. The results suggest why in the earlier room temperature measurements the steep part of the emission edge could not be detected. The premature peak at 0.7 eV below the edge in the emission spectra is not explainable by an ODOS and remains a puzzle.

In order not to add to the already existing confusion we refrain from determining separate numbers for the different broadening mechanisms contributing to the width of the edge by a many parameter fit procedure. Theoretical values for core-hole phonon coupling in Li were calculated by several authors and vary within about an order of magnitude (McAlister 1969, Bergersen et al. 1971,

Dow et al. 1973, Flynn 1976). A very recent calculation (Flynn 1976) based on momentum transfer considerations, however, is in good agreement with experiment and reproduces the observed slight increase of phonon induced width (Baer et al. 1976) when going from the Li K-absorption experiment ($\hbar k = 0.028$ Å^{-1}) to XPS with Al K_α excitation ($\hbar k = 0.75$ Å^{-1}).

A shift of the same order as that given in the last row of Table I was observed in the XPS measurement too (Baer et al. 1976). The emission (Callcott and Arakawa 1977) and the absorption spectra consistently shift by the same amount for all temperatures. The origin of this effect is not yet clear, with respect to a possible relation to phonon emission see Bergersen et al. 1971.

Finally we would like to point out an inconsistency between the XPS - measurements and the shape of the K absorption edge: As mentioned above, the best fit to the edge was obtained by Baer et al., 1976 by a convolution of Gaussian and Lorentzian distributions similar to the corresponding phonon and Auger widths deduced from the XPS experiment with McAlisters one-electron ODCS, which means that a MND threshold exponent (see e.g. Mahan 1974) $\alpha_l = 0$ was assumed. On the other hand, however, the observed asymmetry of the XPS line yields a threshold exponent $\alpha_l = -0.13$ (Baer et al. 1976), which according to the MND power law should give rise to considerable rounding of the ODOS. Quantitative statements cannot be made since the Fourier transform of the time dependent correlation function which gives the absorption spectrum near threshold, has yet only been carried out for a step-like ODOS of the form Θ ($\hbar\omega = E_{threshold}$) (Mahan 1974). Qualitatively, however, it is remarkable, that with $\alpha_l = 0$ no influence of the MND effect is observed. This situation is analogous to that at the Cs N_5-edge: From our EDC measurements on Cs we deduced a threshold exponent $\alpha_l = 0.12$ while the Cs N_5-edge can be explained in the same way as the Li K-edge with a rising p-symmetric ODOS (Petersen 1975b). In the case of Li this deficiency was claimed

to be caused by neglect of spin-dependent effects (Girvin and Hopfield 1976). According to these authors such exchange effects are expected to be strong in Li only and their inclusion leads to $\alpha_l \neq 0$ in that case. This, however, does not explain the analoguous problem at the Cs N_5-edge. As was pointed out by us in a previous paper (Petersen 1975b), XPS line asymmetries and the respective edge shapes can obviously not be both explained consistently within the framework of the MND theory in its present form.

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Table I Widths and relative positions of the Li K absorption edge at different temperatures. All values are given in meV.

Temperature (K)	79	300	370	440	480
Width of total rising part (10-90 %) up to the peak at 55.5 eV Kunz et al. 1974	370/470[a]	530	600	640	770
Edge with (10 % - 90 %)	230	330	400	460	510
Edge with (10 % - 90 %, deduced from Baer et al. 1976)	290	420	500	570	680
Shift of excitation energy to E_F[b] with respect to the 79 K value 54.87 ± 0.05 eV (Petersen 1975a)	-	+10	+50	+90	+100

(a) width of the rising part with the kink (Petersen 1975a)

(b) note that these roughly estimated numbers increase when an E_F-position consistent with Baer et al. "10 % - 90 % values is chosen

Figure captions

Fig. 1 The K-absorption spectrum of Li as measured by Haensel et al. in 1970, included is the K-edge at about 90 K (Kunz et al. 1971).

Fig. 2 Photoyield spectra of solid and liquid Li. The ODOS calculated by Bross 1973 without (ODOS) and with (ODOS + correl.) electron-electron correlations and the calculated atomic cross section σ (McGuire 1970) is included. See text for relative scaling of curves.

Fig. 3 K-absorption threshold for solid and liquid Li. The ODOS calculated by McAlister 1969 and a pseudopotential calculation for the solid and the liquid state (DOS solid/liquid) by Shaw and Smith 1969 are included.

Fig. 4 The onset of the Li K-absorption spectrum at various temperatures. See text for details.

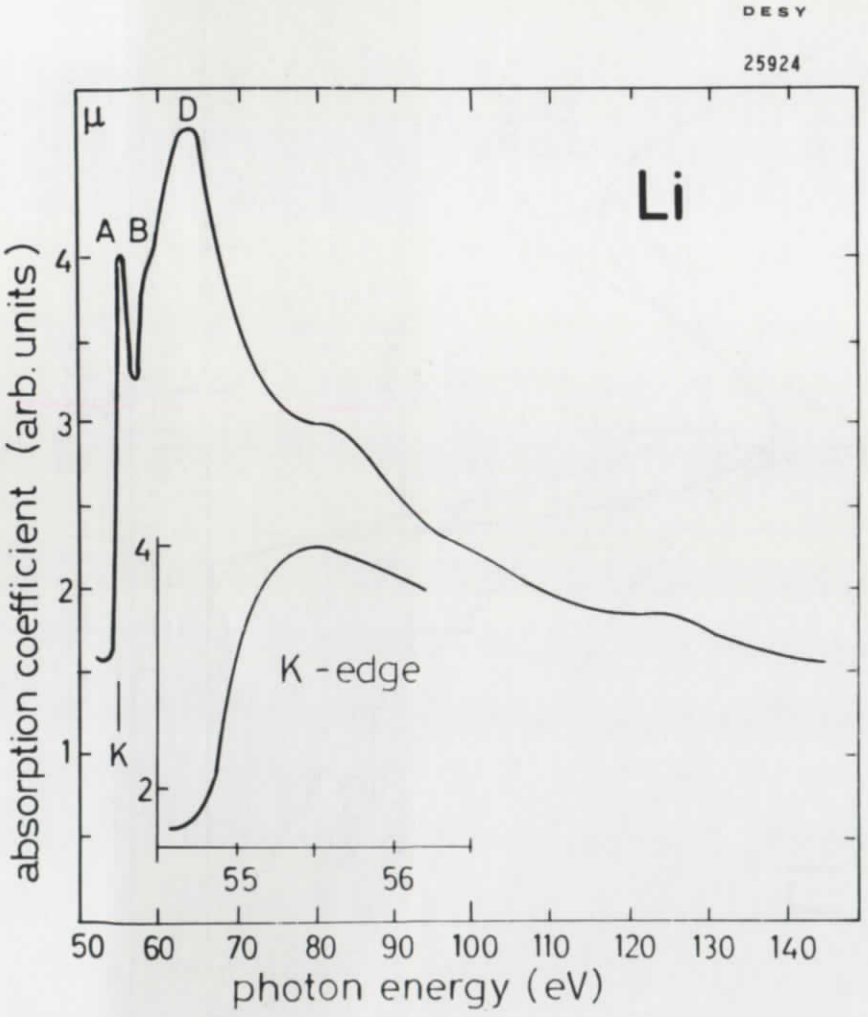
DESY
25924
Li
μ
A B
D
K
K - edge
absorption coefficient (arb. units)
photon energy (eV)
50 60 70 80 90 100 110 120 130 140
55 56

Fig. 1

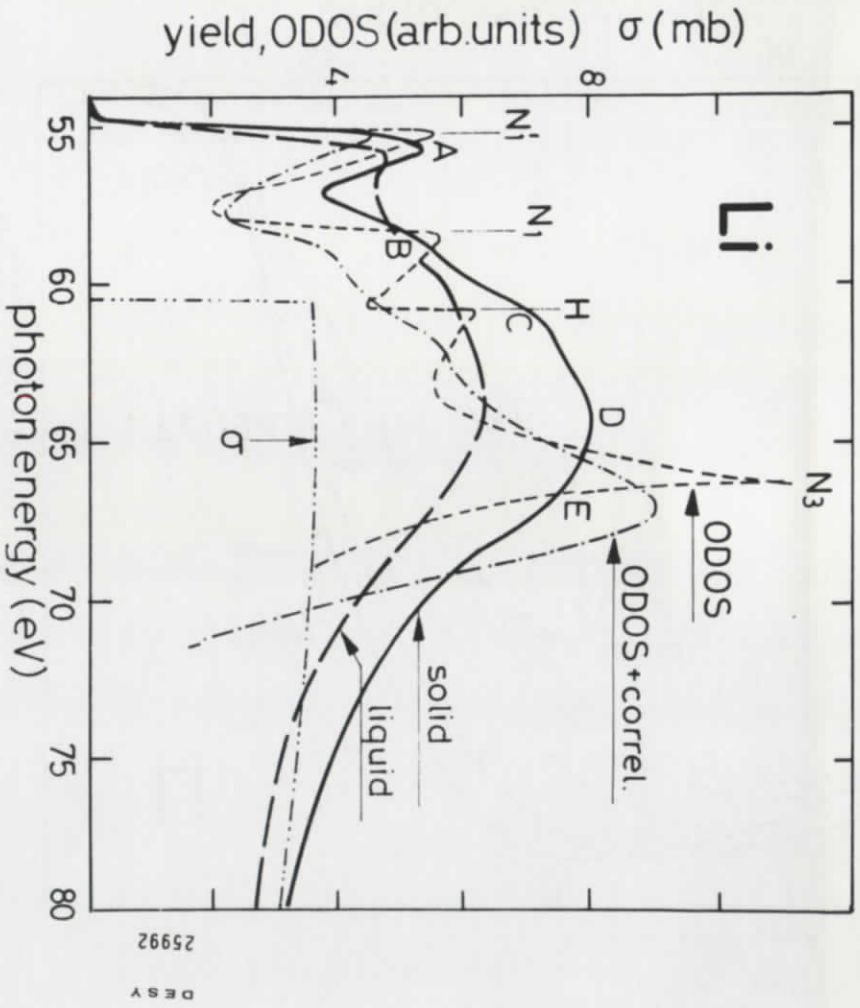
yield, ODOS (arb. units) σ (mb)
Li
A
B
C
D
E
H
σ
ODOS
ODOS+correl.
solid
liquid
photon energy (eV)
55 60 65 70 75 80
4 8
DESY
25992

Fig. 2

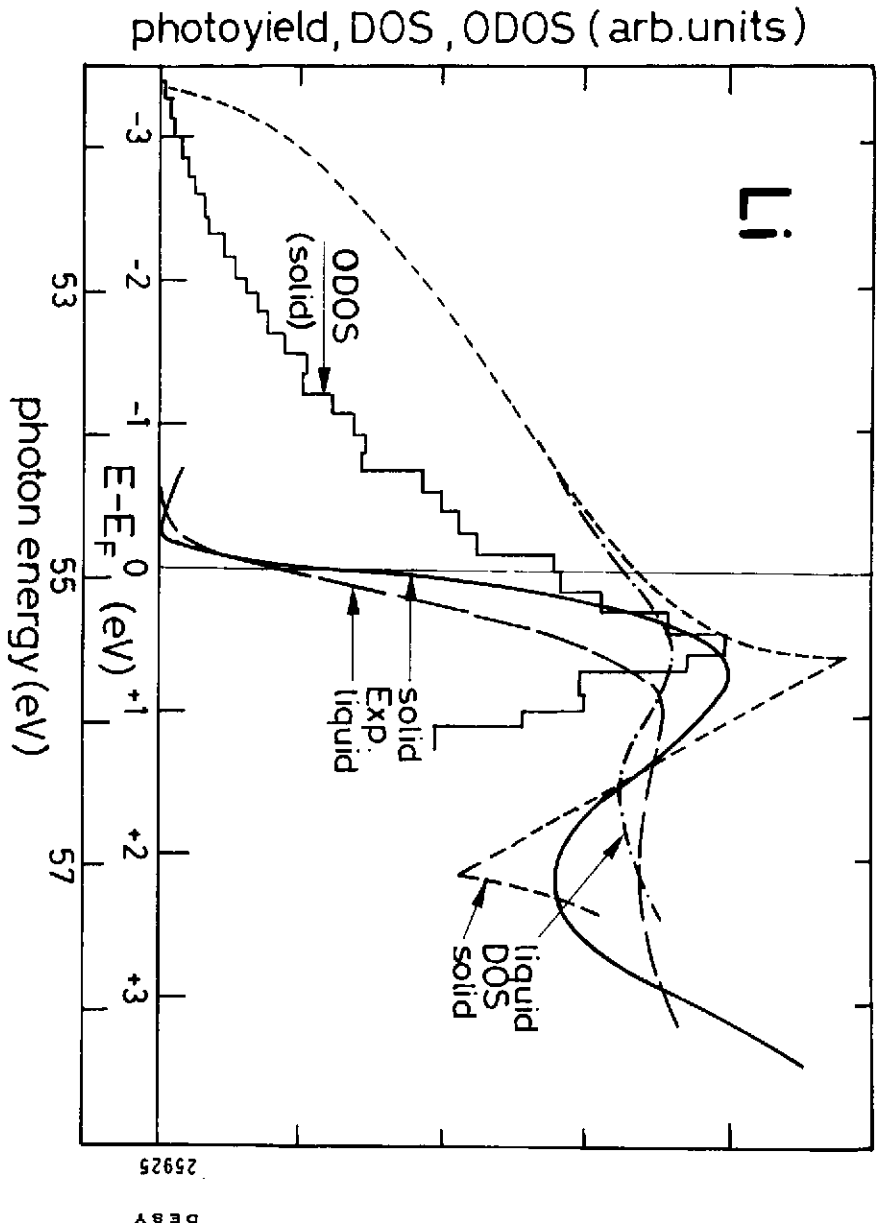
photoyield, DOS , ODOS (arb.units)
Li
ODOS (solid)
solid Exp.
liquid
solid DOS
liquid DOS
photon energy (eV)
E-E_F (eV)
53
55
57
-3
-2
-1
0
+1
+2
+3
25925
DESY

Fig. 3

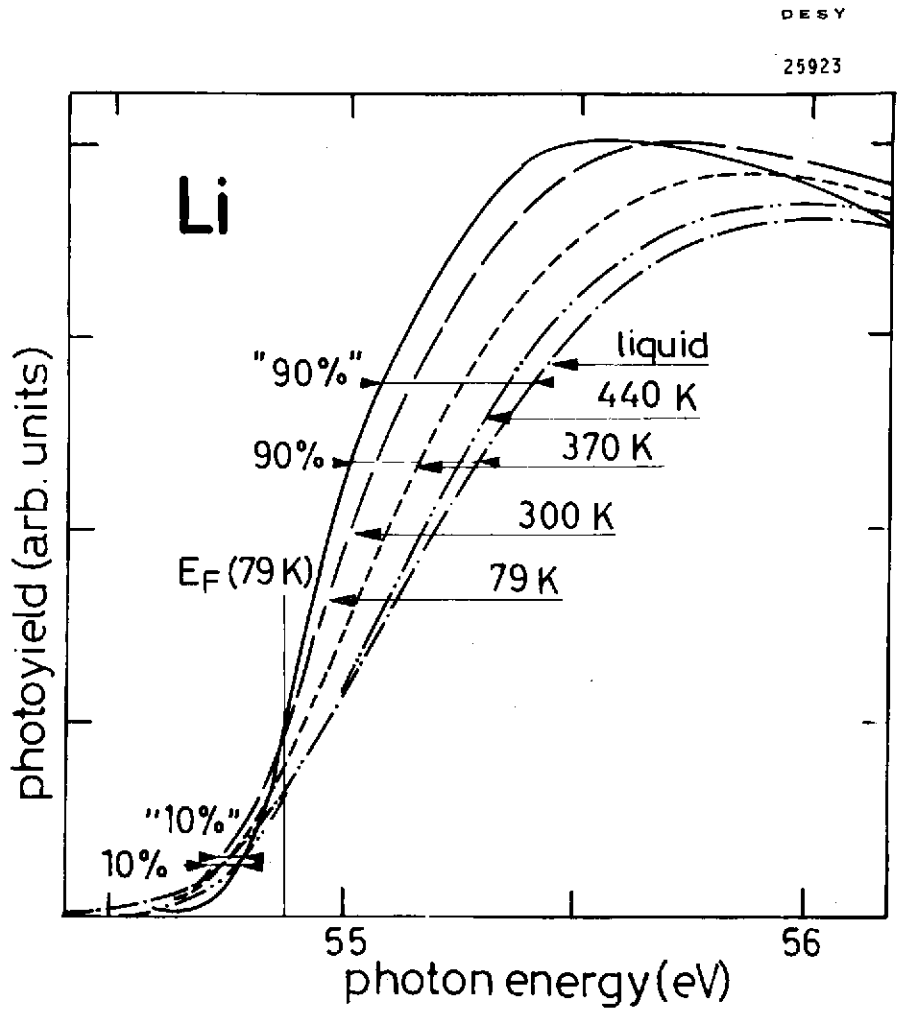
DESY
25923
Li
liquid
"90%"
440 K
90%
370 K
300 K
E_F (79 K)
79 K
"10%"
10%
photoyield (arb. units)
55
56
photon energy (eV)

Fig. 4