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The Temperature Dependence of the K Absorption Edge of Lithium

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The shape of the K absorption edge of Li has been measured at 293 K, 373 K, 443 K and ~480 K (liquid) by photoyield methods. Unpublished transmission data on the shape of the edge at and below room temperature have been reanalyzed. There is a marked increase of the width of the edge with increasing temperature above 293 K, indicating that the lattice plays a major role in the broadening of the edge.

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The explanation of the shapes of the K absorption and emission edges in Li (and L edges in several other light metals) is a subject of considerable recent controversy. The apparent depression from the expected relatively sharp Fermi step has been explained as a many-body effect[1-3] in which a depression is expected for $s \rightarrow p$ transitions in absorption, e. g., the Li K edge, and an enhancement ("spike") expected for absorptive $p \rightarrow s$ transitions, e. g., the Na $L_{2,3}$ edge. Dow and co-workers[4-6] have disagreed with the many-body explanation for the Li K edge, proposing that a simpler model explains the shape of the edge. The rounding of the K edge in Li is then the result of a broadening of the initial 1s electron level by the indirect interaction with phonons (via the 2s electrons)[5], or a lifetime broadening of the 1s hole by Auger transitions[6], or both. The Auger transition rate, if large enough to dominate, would be very sensitive to the 2s wave function amplitude at the hole site. It may therefore depend on temperature. Since the electron-phonon interaction should lead to a measureable temperature dependence of the edge, and the Auger processes also might do so, measurements of the temperature dependence of the edge are clearly important. Moreover, a strong temperature dependence at higher temperatures could imply that at least part of the low temperature width is due to zero-point vibrations, and is not entirely a many-body effect. Such measurements are reported herein.

In addition to the published[7] values at $\sim$77 K, unpublished absorption measurements at and below 300 K were made in this laboratory[8] in 1970. A 2-m Rowland-mount monochromator and the synchrotron radiation from the Deutsches Elektronen-Synchrotron were used[7]. The resolution at 50 eV was

0.03 eV. The pressure in the sample chamber was about 10^{-6} Torr during evaporation and measurements. The samples were surrounded by a radiation shield which served to protect the films from water molecules, which enhance the rate of oxidation. The temperature of the sample mount was measured with a thermocouple to be 4.2 and 77 K, but the film temperatureswere probably some 5 - 10 K higher. The transmission spectra were converted to absorption coefficient spectra. The data taken at 300 K were on films in various states of oxidation and are the least representative of clean Li. In this case a superposition of metal and oxide spectra was observed. Therefore from these data no accurate edge width could be obtained.

The present measurements at and above 293 K were of the photoyield of massive specimens of Li. The photoyield has been shown to be proportional to the absorption coefficient, except for the shape of the smoothly varying background[9,10]. The light source was DESY and a recently designed monochromator especially suited to such a source[11]. The resolution was <0.15 eV at 50 eV. The calibration was accurate to ±0.2 eV. The photoemitted electrons were passed through a retarding field and a spherical plate energy analyzer[12]. The 2 eV resolution of the analyzer does not affect our measurements, for only the inelastically-scattered electrons are measured, which are taken as representative of the yield. Scans of the yield spectrum were made at several values of the retarding potential to permit removal of the structure due to the unscattered electrons directly emitted from the K level. The samples were pieces of solid Li placed on a Ta strip. A thermocouple was inserted into the melt under Ar protection before evacuating the system. After bake-out and cryopumping, when the pressure was in the $1\text{-}8\times10^{-10}$ Torr range, the sample was melted, then scraped and stirred with a W brush. This moved macro-

scopic pieces of oxide aside or made them sink into the melt. Clean liquid Li, once obtained, could be maintained for several hours. The solid Li was cleaned by scraping with the W brush. At a measured pressure of 1.3×10^{-10} Torr the Li remained free of oxide for about 2 hours. Thereafter indications of oxide could be observed. The oxidation was monitored by measuring the ratio of the edge discontinuity with respect to the signal below the edge (4.5:1 was our best value; it decreases with oxidation). Another indication of oxide is a peak emerging at 58 eV.

Figure 1 shows the absorption edge. The edge at 77 K has been published previously[7], but a remeasurement[8] gives the edge as shown in Fig. 1, shifted with respect to the older measurements to higher energy (by .16 eV). The 50 % position of the edge at 77 K and at 4 K is 54.86±0.15 eV. The shape of the absorption spectrum above the edge has been published elsewhere[7,12]. The yield spectroscopy data show a shift of the edge to higher energies by 0.06 eV between 293 K and 443 K. There is a further shift of 0.12 eV upon melting. The shift between 4 K and 293 K is also to higher energies, but difficult to estimate because two different monochromators were used.

The 10 % to 90 % width of the edge (ΔW) as a function of temperature is plotted in Fig. 2. Below room temperature we are in disagreement with a value obtained with an energy loss technique by Ritsko et al.[15]. In contrast to Ritsko et al.[15] we did not attempt to make a deconvolution of our measurements since we believe that the accuracy of such a procedure is usually low. In order to be consistent we used their raw data value of the edge widths at both temperatures.

It is clear that there is a large, temperature-dependent broadening of the edge. The theoretical estimate by Dow et al.[5] of the phonon broadening of the 1s levels gives the width of the edge as proportional to the rms lattice displacements, which have been measured by Smith et al.[13] A plot of the measured width of the Li K edge vs. rms displacement is shown in Fig. 3. The yield data fall on a reasonably good straight line. The width of the Fermi function is too small to be a dominant feature on the width. This does not, necessarily verify the electron-phonon interaction model for the broadening, for the Auger mechanism may also have a similar dependence[6]. Figure 3 does, however, demonstrate that phonons are involved in the broadening mechanism. If phonon coupling to the 1s electrons is the sole broadening mechanism, the slope of the line in Fig. 3, 1.3 eV/Å, is a measure of the coupling constant. This must be viewed with caution, for the displacement used for Fig. 3 are total displacements, involving phonons from all branches, while the 1s electron will couple to different phonon branches with different weights. The generally looser structure of the liquid ought to account for the discontinuity of the width at the MP. We are not aware of any measurements of the mean square displacement in liquid Li.

Our measurements have demonstrated that there is a temperature dependence of the width of the K absorption edge in Li, one that varies roughly as the rms lattice displacement. A possible explanation of the temperature dependence is the phonon-broadening model of Dow et al.[5] One also must examine the effect of lattice vibrations on the Auger width of the 1s hole[6]. The many-body calculation has not been carried out extensively at finite temperature, but it has been

estimated[14] as being approximately independent of temperature. It seems clear from Fig. 3 that at 0 K, zero-point lattice vibrations account for at least part of the width, making the role of many-body effects smaller than previously believed.

We wish to acknowledge many lively discussions with J.D. Dow. One of us (DWL) wishes to thank the II. Institut für Experimentalphysik, Universität Hamburg, for financial support.

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Figure Captions

Fig. 1: Li K edge at different temperatures. The curve at 4 K was obtained by absorption measurements, the other curves by yield spectroscopy. The 50 % values of the edges of two curves not drawn at 77 K (absorption) and at 373 K (yield) are 54.87 eV and 55.03 eV, respectively. The curves are scaled to the same amplitudes. All the yield curves coincide with the dashed curve below 54.5 eV.

Fig. 2: Li K edge with ΔW vs. temperature, MP = melting point (452 K)

Fig. 3: Li K edge with ΔW vs. rms lattice displacement[13] δR. The straight line is an interpolation of the high amplitude values.

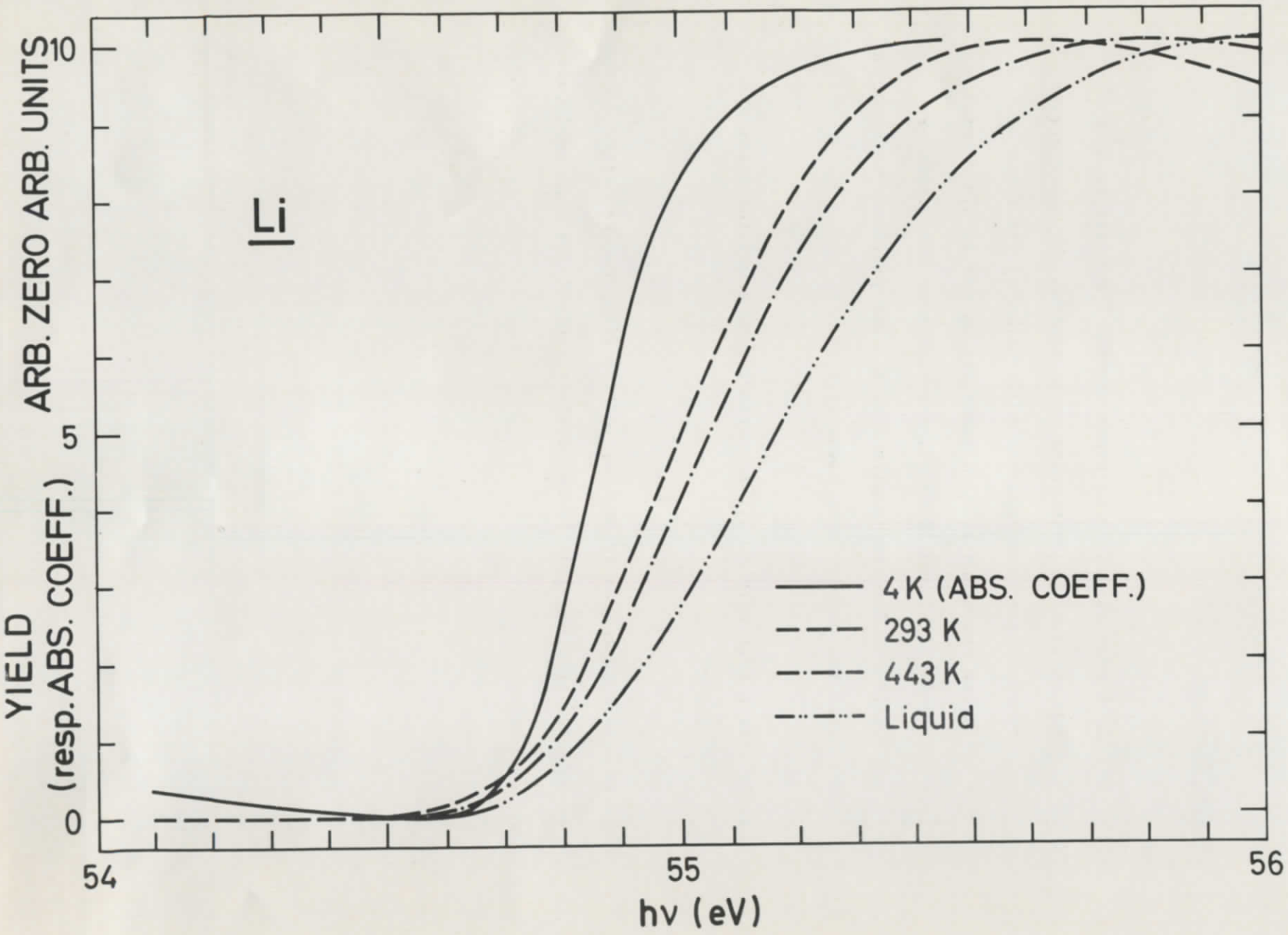
Li
YIELD
(resp. ABS. COEFF.)
ARB. ZERO ARB. UNITS
0
5
10
54
55
56
hν (eV)
4K (ABS. COEFF.)
293 K
443 K
Liquid

Fig. 1

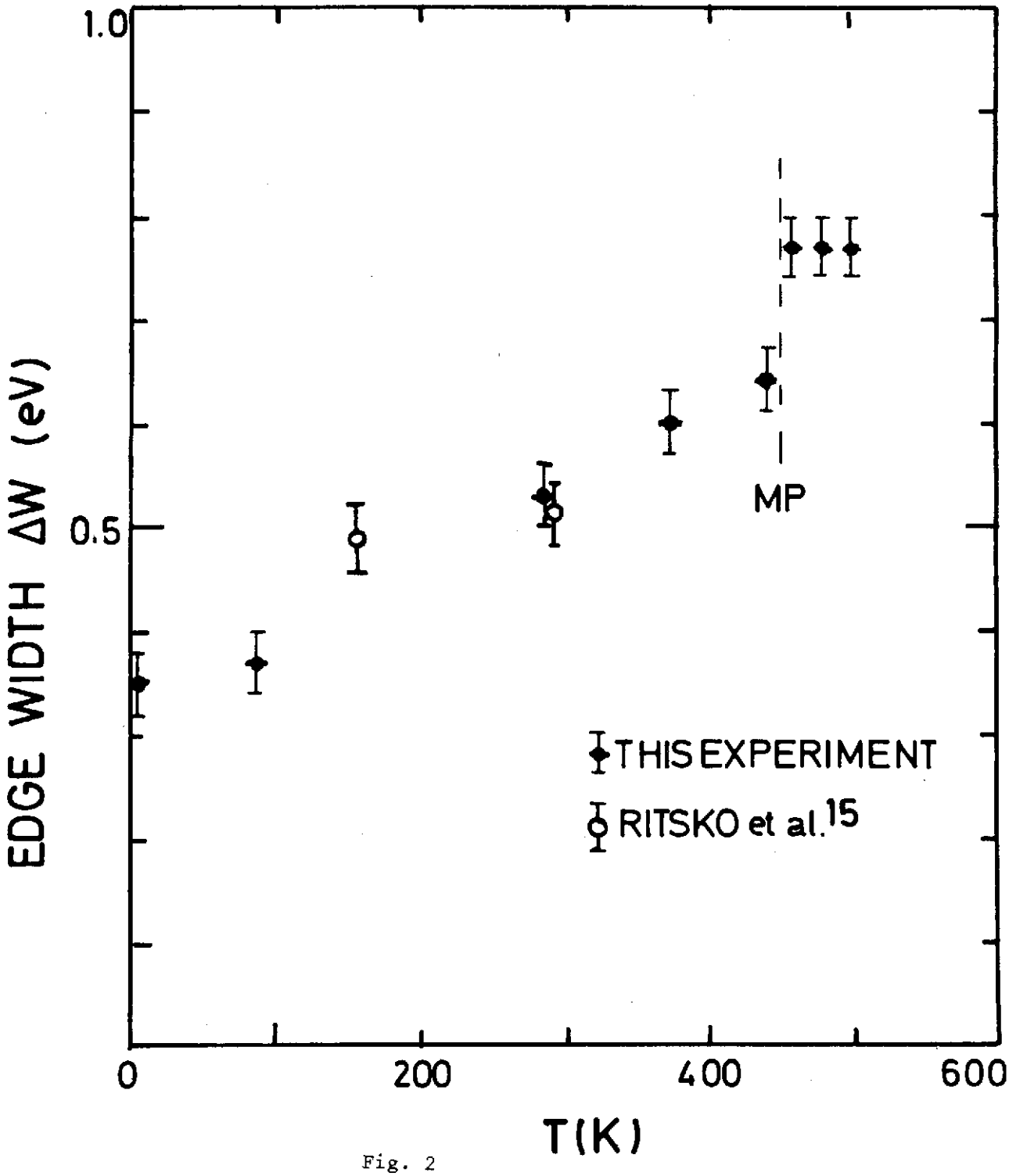
1.0
0.5
EDGE WIDTH ΔW (eV)
MP
THIS EXPERIMENT
RITSKO et al.[15]
0
200
400
600
T(K)

Fig. 2

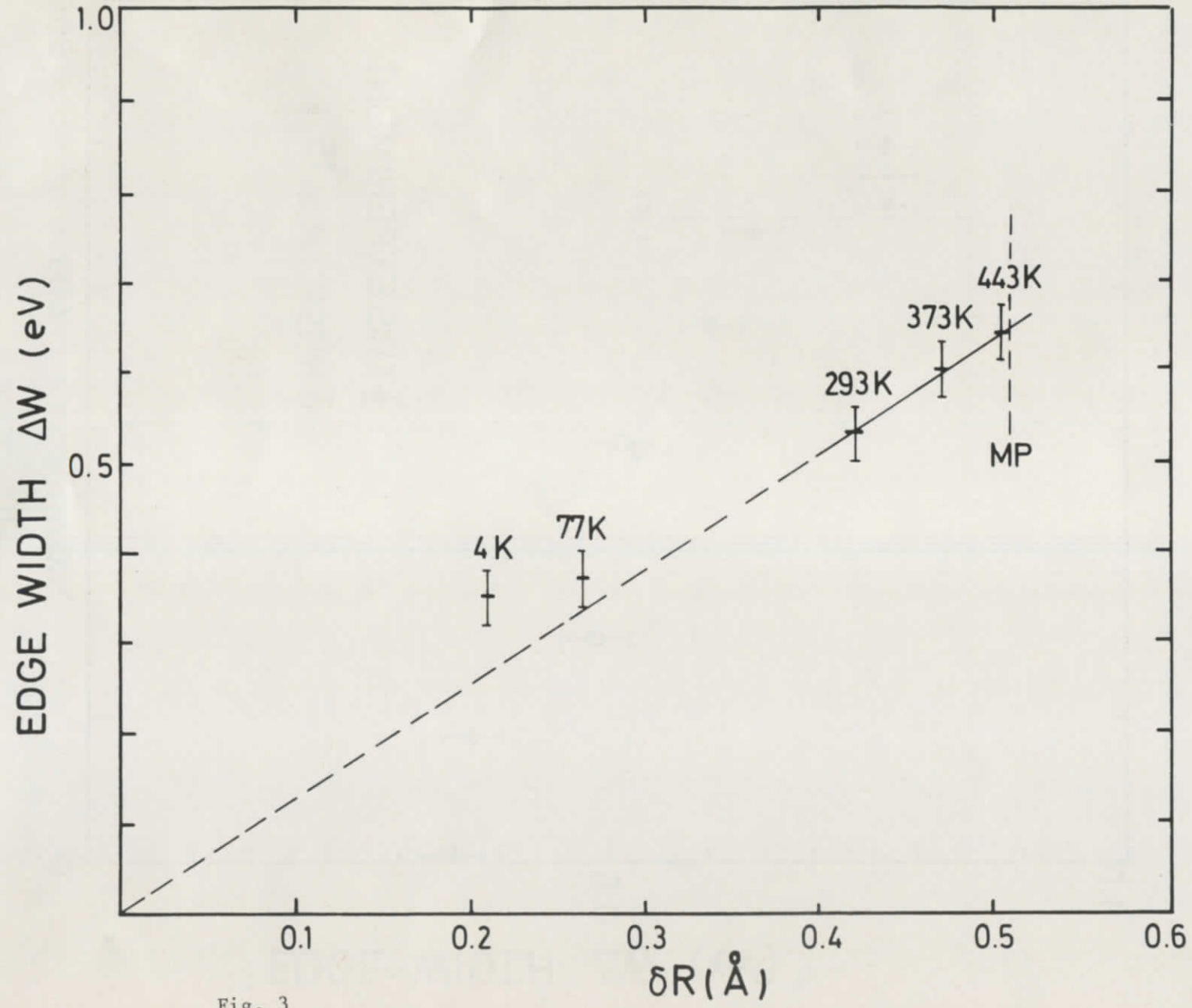
1.0
0.5
EDGE WIDTH ΔW (eV)
4K
77K
293K
373K
443K
MP
0.1
0.2
0.3
0.4
0.5
0.6
δR(Å)

Fig. 3