Temperature Dependence of the K Absorption Edge of Lithium

C. Kunz
Deutsches Elektronen-Synchrotron

H. Petersen
Deutsches Elektronen-Synchrotron

David W. Lynch
Iowa State University, dlynch@iastate.edu
Temperature Dependence of the K Absorption Edge of Lithium

Abstract
The shape of the K absorption edge of Li has been measured at 293, 373, 443, 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 Unpublished transmission data on the shape of the edge at and below room temperature have been reanalyzed.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.

Keywords
photoyield, emission edge, Ames Laboratory

Disciplines
Atomic, Molecular and Optical Physics | Physics

Comments
Temperature Dependence of the $K$ Absorption Edge of Lithium

C. Kunz and H. Petersen

Deutsches Elektronen-Synchrotron, 2000 Hamburg 52, Germany

and

D. W. Lynch

Ames Laboratory—USAEC, and Department of Physics, Iowa State University, Ames, Iowa 50010, and
II. Institut für Experimentalphysik, Universität Hamburg, 2000 Hamburg 50, Germany

(Received 21 October 1974)

The shape of the $K$ absorption edge of Li has been measured at 293, 373, 443, and $\sim 480$ 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 Unpublished transmission data on the shape of the edge at and below room temperature have been reanalyzed.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.

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 in which a depression is expected for $s-p$ transitions in absorption, e.g., the Li $K$ edge, and an enhancement ("spike") expected for absorptive $p-s$ transitions, e.g., the Na $L_{1,2}$ edge. Dow and co-workers have disagreed with the many-body explanation for the Li $K$ edge, proposing that a simpler model explains the rounding of the edge. While earlier attempts to calculate the broadening of the initial $1s$ electron level by a direct interaction with the phonons in the most sophisticated version yielded small values at room temperature ($\approx 0.1$ eV), Dow, Robinson, and Carver propose a stronger indirect interaction mediated by the $2s$ electrons, which in a first rough estimate appeared to confirm the experimental edge width ($\approx 0.5$ eV). Another possible source of the edge broadening is the lifetime of the $1s$ hole due to Auger transitions.

The many-body theory is an essentially temperature-independent mechanism; the Auger broadening has a temperature-independent base width at zero temperature and could possibly contain also a temperature-dependent term from the oscillating $2s$ wave-function amplitude at the hole site. If the direct or the indirect interaction of the core hole with phonons was responsible for the edge width a strong temperature dependence is expected to show up. Therefore measurements of the edge width as a function of temperature are clearly important. Such measurements are reported herein.

In addition to the published values at $\sim 77$ K, unpublished absorption measurements at and below 300 K were made in this laboratory. A 2-m Rowland-mount monochromator and the synchrotron radiation from DESY were used. The resolution at 50 eV was 0.03 eV. The pressure in the sample chamber was about $10^{-5}$ 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 temperatures were 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 clear 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. The light source was DESY and a recently designed monochromator especially suited to such a source. The resolution was $< 0.15$ at 50 eV. The calibration was accurate to $\pm 0.2$ eV. The photoemitted electrons were passed through a retarding field and a spherical-plate energy analyzer. 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 val-
ues 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 bakeout and cryopumping, when the pressure was in the $(1-8) \times 10^{-10}$ Torr range, the sample was melted, then scraped and stirred with a W brush. This moved macroscopic 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 $1.3 \times 10^{-10}$ Torr the Li remained free of oxide for about 2 h. 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, but a re-measurement gives the edge as shown in Fig. 1, shifted with respect to the older measurements to higher energy (by 0.16 eV). The 50% position of the edge at 77 and at 4 K is 54.86 ± 0.15 eV. The shape of the absorption spectrum above the edge has been published elsewhere. The yield-spectroscopy data show a shift of the edge to higher energies by 0.06 eV between 293 and 443 K. There is a further shift of 0.12 eV upon melting. The shift between 4 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 ($\Delta W$) 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, Schnatterly, and Gibbons. In contrast to Ritsko, Schnatterly, and Gibbons 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, Robinson, and Carver 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. A plot of the measured width of the Li $K$ edge versus 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. Our result does not necessarily verify the electron-phonon interaction model for the
broadening, for other models involving phonons will have a similar dependence.\(^4\) 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 displacements 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 melting point. 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, Robinson, and Carver\(^5\). 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\(^7\) 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 (D. W. L.) wishes to thank the II. Institut für Experimentalphysik, Universität Hamburg, for financial support.

\(\text{FIG. 3. LiK edge width } \Delta W \text{ versus rms lattice displacement (Ref. 14) } \delta R. \text{ The straight line is an interpolation of the high-amplitude values.}\)

\(^{*}\text{Permanent address.}\)


