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# Emission and absorption x-ray edges of Li†

T.A. Callcott* and E. T. Arakawa
*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*

D. L. Ederer
*Synchrotron Ultraviolet Radiation Facility, National Bureau of Standards, Washington, D. C. 20234*

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The *K* x-ray emission edge of Li is measured between 85 and 490 K and analyzed to obtain the temperature dependences of the edge position and of a Gaussian edge-broadening function. Full width at half-maximum edge widths range from $0.22 \pm 0.05$ eV at 85 K to $0.38 \pm 0.05$ eV at 440 K. Edge positions shift from $54.81 \pm 0.02$ eV at 85 K to $54.86 \pm 0.02$ eV at 440 K and to $54.91 \pm 0.02$ eV after melting. Emission and absorption spectra measured with the same spectrometer establish a $0.10 \pm 0.02$ eV separation between the emission and absorption edges. These results are compared with recent theories describing incomplete lattice relaxation about the core hole. We conclude that for a core-hole lifetime of 0.016 to 0.030 eV the theories give a satisfactory explanation of the premature peak in the emission spectra. We suggest also that phonon–core-hole interactions provide the dominant edge-broadening mechanism, and that many-body effects are small.

## I. INTRODUCTION

In a recent paper, two of the present authors (Callcott and Arakawa) presented data on the temperature dependence of the *K* x-ray emission edge of Li. The results demonstrated that the very broad emission edge observed above room temperature could be resolved at low temperatures into a steep high-energy edge plus a peak lying about 0.7 eV below the edge.[1] Similar results had been reported earlier by Crisp and others,[2–4] but in recent years had generally been attributed to a very broad emission edge modified by self-absorption.[5–8] We argued that internal evidence in the data and our choice of experimental parameters eliminated the possibility that self-absorption was an important factor determining the edge shape. The more detailed analysis of this paper will give further support to this conclusion.

While the initial paper was being processed for publication, Almbladh and Mahan, working independently of each other and without knowledge of our results, completed essentially equivalent theoretical treatments that give a satisfactory explanation of the experimental results.[9,10] In these calculations, the observed shape is produced when the lifetime of the core hole created by absorption is comparable with the relaxation time of the lattice about the hole.

In this paper, we have a threefold purpose. First, we report the results of a more careful analysis of the emission-edge data which yields a more accurate measure of the breadth of the emission edge and of its energy position as a function of temperature. Second, we present new measurements of both the absorption and emission edges performed in the same vacuum system and with the same spectrometer at the National Bureau of Standards (NBS) electron storage ring. These measurements determine unambiguously the relative positions of absorption and emission edges without any question of instrumental calibration. Finally, we compare the emission-edge shape and the separation between the emission and absorption edges with the new theoretical calculations of Almbladh and Mahan. From the comparisons we obtain values of the phonon broadening and core-hole lifetime of Li which are compared with values obtained from absorption-edge and photoemission data by other authors.[11–14] We conclude that the theory satisfactorily accounts for the shape of the Li x-ray edges without any important contribution from many-body effects.

## II. EXPERIMENTAL APPARATUS AND PROCEDURES

The temperature dependence of the emission spectra was measured in the apparatus shown schematically in Fig. 1. In most of the measurements a defocused 4–6-mA beam of 2-kV electrons was incident on the sample at 45°. In experiments to check for possible self-absorption effects, beam energies of 1000 V and an angle of incidence of about 70° from the normal were used, but no differences were seen in the emission spectra. The sample substrate was the flat end of a 1-in.-diam hollow Cu cylinder which was cooled internally by circulating fluid. Liquid nitrogen, dry ice in methanol, and ice water were used to establish temperatures below room temperature. At room temperature and above, compressed-air cooling and electron-beam heating were used to

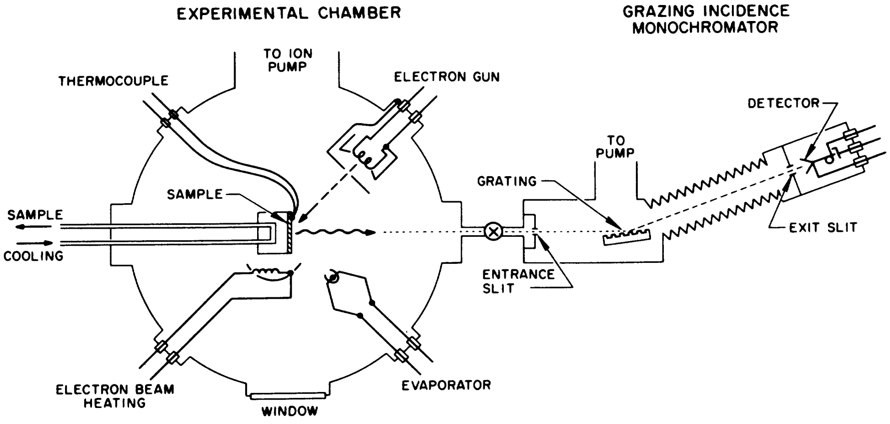

FIG. 1. Experimental apparatus for emission measurements.

establish the desired temperature. Temperature was measured by an iron-Constantan thermocouple clamped against the emitting surface with a screw. We estimate that the indicated temperatures are accurate to ±5 K. The measured temperature at the instant of melting was within 3° of the melting point of Li.

Li wire (99.95%), originally stored in mineral oil, was cleaned by rinsing in acetone, scraping off accumulated oxides and hydroxides, and etching in dry methyl alcohol. It was loaded into a tantalum boat and installed in the vacuum chamber immediately before pumpdown. Final cleaning and outgassing were accomplished by heating the boat to evaporation temperature during a mild bakeout of the vacuum system.

The base pressure of the ion-pumped system after bakeout was $(1-2)\times 10^{-8}$ Torr as measured by a nude ion gauge in the chamber. Typically the pressure rose to $(1-3)\times 10^{-7}$ Torr during evaporation of Li. Measurements were made at pressures of $(4-6)\times 10^{-8}$ Torr, which was the steady-state system pressure with the spectrometer valve open and the electron gun delivering a 10 W beam to the sample surface (2 kV, 5 mA).

The emission intensity from a freshly evaporated Li surface decreased slowly with time (typically to 80% of initial intensity after 2 h of measurements), but did not change in spectral shape or energy position. One film was remeasured after storage at the system base pressure for 5 d . Its intensity had decreased to about 30% of the initial intensity, but the shape and position of the emission edge were unchanged. For evaporations performed before thorough outgassing of the Li, a prominent lithium oxide or hydroxide peak is observed just below the Li peak. Some emission was observed in this region after long storage of the Li film in vacuum, but was never more than 10% of the true Li emission peak.

Measurements were made with a McPherson Model 247 2-m grazing incidence spectrometer fitted with a stainless-steel entrance-slit assembly, a gold-coated 600 lines/mm grating, and a channeltron detector. The instrument was calibrated using the spark spectrum of air which produces a large number of narrow spectral lines between 150 and 500 Å (25–80 eV). Resolution was directly measured from the half-width of single lines in the spark spectrum. The calibration is believed to be accurate to 0.03 eV.

Measurements of the channeltron current were made with a picoammeter whose output was digitized at 2-sec intervals. At high resolution ($\sim$0.1 eV), the measured spectra were quite noisy, and data from 15 or 20 separate measurements of the spectra were averaged to obtain the published emission curve for each temperature.

The combined emission and absorption measurements were made in a cryo-pumped vacuum chamber in the beam line between the electron storage ring at the NBS and a 3-m grazing incidence spectrometer. This geometry dictated that the absorption measurements be made by illuminating the Li film with continuum radiation from the accelerator and measuring the transmitted radiation as a function of wavelength. The $K$-emission spectrum was measured by lowering the emission target into the beam line so that its emitting surface faced the entrance slit of the spectrometer. The characteristics of the storage ring, beam line, and spectrometer have been described elsewhere.[15] The spectrometer was used with a 600 lines/mm gold-coated concave grating, 25-$\mu$m slits, and a channeltron detector. The full-width-at-half-maximum (FWHM) resolution was 0.14 Å (0.034 eV at 55 eV), and the wavelength calibration is believed to be accurate to 0.03 eV. Measurements were made at a measured chamber pressure of about $1\times 10^{-7}$ Torr.

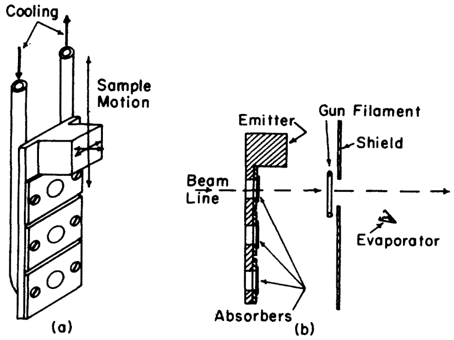

FIG. 2. (a) Sample mount for combined emission and absorption measurements. (b) Experimental arrangement of sample, evaporator, and electron gun for the combined measurements.

Because of space limitations in the experimental chamber, an evaporator, electron gun, and a combination sample holder for both emission and absorption measurements were assembled on a single $4\frac{1}{2}$-in.-o.d. Conflat flange. The sample holder is shown in Fig. 2(a) and a schematic of the experimental assembly in Fig. 2(b). The liquid-cooled sample holder had a 2-in. vertical ($Z$) motion and could be moved within a $\frac{1}{2}$-in.-diam circle in the $X$-$Y$ plane. Three carbon film absorption substrates were mounted on the lower part of the sample holder and a Cu anode block was located at the top. By moving the sample holder up and down, the anode or the absorption substrates could be placed in position to receive evaporated Li, or in the beamline so that they filled the entrance aperture of the spectrometer.

Electrons from a $W$ filament were used to excite the $K$-emission spectrum from Li evaporated onto the liquid-nitrogen-cooled anode. The shield between filament and evaporator served both as an electron reflector for the electron "gun" and as an evaporation shield. The emission data published here were taken with −1500 V on the emitting filament and shield and +600 V on the sample. These settings were found by trial and error to give maximum emission from the sample with a total "gun" voltage of about 2 kV. During emission measurements a 6-mA beam current was maintained on the sample by adjusting the filament current.

For the measurements at NBS, pulse counting techniques were used to accumulate the channeltron output. The sweep rate of the wavelength drive and the dwell time on each channel of the multichannel scalar were both controlled by the beam monitor of the storage ring so that each channel represents both a constant wavelength interval and a constant incident number of photons on the Li film.[15] Neglecting background counts, this recording system accurately compensates for the slowly decreasing intensity of light from the storage ring. In practice, the collection interval is printed out along with the number of counts per channel so that a correction can be made for the background count.

1000-Å carbon films supported on 80% transparent mesh were used as substrates for the absorption measurements. Transmittance was obtained by dividing the transmitted intensity of the substrate plus Li by the transmitted intensity of the substrate alone. Li slowly evaporated onto the cooled carbon substrates produced specular films that had a single sharp absorption edge. After several hours this edge would broaden and shift in energy as the films began to oxidize.

## III. EXPERIMENTAL RESULTS

The $K$-edge emission spectra at 85 and 400 K are presented in Figs. 3 and 4. These are two of five measurements of the Li edge made with an instrumental resolution of 0.11 eV at approximately equal temperature intervals between 85 and 493 K. The data points represent averaged values from 15 measurements of the emission edge taken on the same film at a fixed temperature over a period of about 45 min. The data are arbitrarily scaled to give a peak value of 1 for a smoothed curve drawn through the data points.

The smooth solid curve drawn through the data points in Fig. 3 was obtained by convoluting the dashed curve having a sharp peak at 54.06 eV and a sharp edge at 54.81 eV with a Gaussian-broadening function to obtain the best fit to the data. The unbroadened dashed curve was selected to obtain a good fit to the upper edge of the 85-K data. In

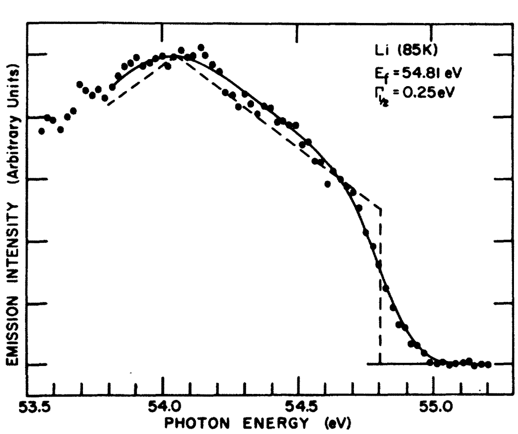

FIG. 3. X-ray emission edge of Li at 85 K. Dashed line is unbroadened edge. Solid line is edge broadened by Gaussian function with a FWHM value of 0.25 eV.

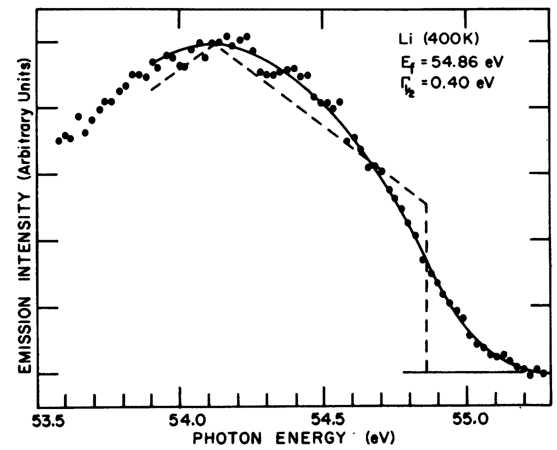

FIG. 4. X-ray emission edge of Li at 400 K. Dashed line is same unbroadened edge function shown in Fig. 3, but moved up in energy by 0.05 eV.

the figures the dashed and solid curve are normalized to one at the peak. The same unbroadened curve was then used to fit data taken at higher temperatures. In all cases, we found it possible to obtain a good fit by adjusting the width of the Gaussian function and the position of the high-energy edge. The fit at 400 K shown in Fig. 4 is typical of those obtained at all higher temperatures.

Plots of the energy position of the edge and of the FWHM width of the Gaussian function as a function of temperature are shown in Fig. 5. Part of the broadening may be attributed to the instrumental resolution. The dashed line of Fig. 5 represents the true broadening remaining after the instrumental broadening has been removed according to the prescription

$$\Gamma_{\rm true}^2 = \Gamma_{\rm total}^2 - \Gamma_{\rm inst}^2 ,$$

where $\Gamma_{\rm inst} = 0.11$ eV is the FWHM resolution of the spectrometer. These temperature dependences are reproducible and have been confirmed by other experimental runs.

The edge width increases with temperature but seems to saturate at a FWHM breadth of about 0.40 eV. No measurable additional change in the width is observed as the film melts. The edge widths of both the emission and absorption spectra of Li have been extensively discussed in the literature. Comparison of our results with other measurements and with theory will be made later in the paper.

Above 300 K, the photon energy of the edge position increases approximately linearly with temperature (slope $\simeq 10^{-4}$ eV/K), but the variation with temperature is much weaker at lower temperatures. This flattening of the curve below 200 K is in agreement with the measurements of Crisp who found little shift in the edge position below liquid-nitrogen temperature.[4] A discontinuous shift in the edge position of about 0.04 eV is observed as the film melts. Our measurements of the shift of the edge position as a function of temperature are similar to those reported by Kunz, Peterson, and Lynch for the absorption edge.[12] A detailed quantitative comparison of our results with their results is difficult because no attempt was (or could be) made in their analysis to deconvolute the true edge broadening from the density-of-states variation that was reported in a later paper.[13] To our knowledge, no theoretical discussion of the change of edge position with temperature has appeared in the literature. Since the shifts in energy position occur in both emission and absorption spectra, it seems probable that the shift can be attributed to small changes in the electronic energy levels as the lattice dilates with increasing temperature. We note in support of this assertion that the curve of the thermal linear expansion of Li has the same shape as the edge position curve.[16] In fact the curve drawn through the edge shifts in Fig. 5 is drawn to be proportional to the published linear expansion of Li.

In Fig. 6 we have plotted the reduced emission and absorption data obtained at the NBS storage ring. The quantities plotted are normalized to unity at their maxima. In order to present the data in a form where intensity is proportional to the density of states, the raw emission data has been divided by $E^5$, where $E$ is the photon energy. This factor is included to account for a factor of $E^3$ which appears in the transition probability and for an additional factor of $E^2$ that results from the fact that the monochromator has a constant-wave-

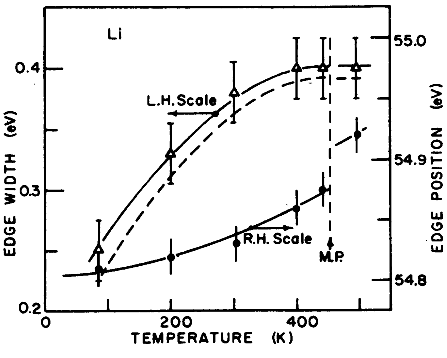

FIG. 5. Temperature dependence of the emission-edge position and width. The width plotted is the FWHM value of the Gaussian function used to fit unbroadened edge to the emission data. Dashed line shows the width after correction for instrumental broadening.

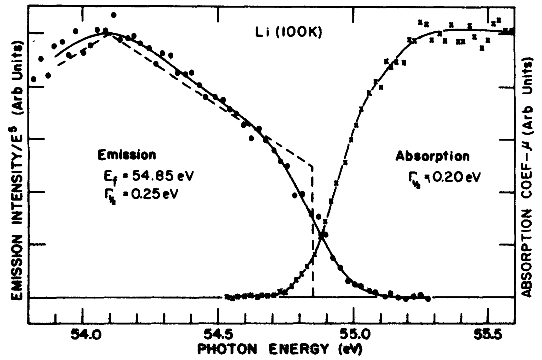

FIG. 6. Emission and absorption edge spectra taken with the NBS spectrometer reduced to be proportional to the density of states. See text for details.

length resolution rather than a constant-energy resolution.[17] In absorption measurements, transmitted intensity is given by $I = I_0 \exp(-\mu d)$. $I$ and $I_0$ are the intensities transmitted by the carbon film and spectrometer with and without the lithium film, respectively. In Fig. 6 we plot $\mu d = \ln(I_0/I)$, since $\mu$ itself is proportional to the density of states. The smooth curve drawn through the emission data is exactly the same curve as that drawn through the emission data of Fig. 3 except that it has been shifted to higher energies by 0.04 eV. This represents the calibration difference between the Oak Ridge National Laboratory (ORNL) and NBS spectrometers. A close examination of the edge suggests that this edge is slightly broader than that shown in Fig. 3, indicating a slightly higher temperature. This is not surprising since in the NBS chamber there was a longer conduction path between the emitting surface, which was receiving 12 W of power, and the cooling coil brazed to the back side of the sample. The precise temperature of the absorbing film is similarly uncertain. Cooling of the film is very inefficient since it occurs by conduction through the thin carbon supporting film and Ni mesh. Fortunately, the power inputs from the photon beam and thermal radiation from the chamber walls are also small so a large temperature rise is not expected. We feel safe in assigning temperatures for both sets of measurements to the range 80–120 K. The exact value of the temperature is not critical because, as we have seen in Fig. 5, the edge position is not very sensitive to temperature below 200 K. The uncertainty in relative edge positions due to differences of temperatures between emitting and absorbing films is no more than about 0.01 eV.

If we take the edge separation between points of maximum slope on the steep edges of the emission and absorption spectra, we find a separation of 0.10 ± 0.02 eV. This value will be compared with available calculations in Sec. IV.

## IV. DISCUSSION OF RESULTS AND COMPARISON WITH THEORY

Before proceeding with a discussion of the results, we briefly summarize the evidence against an explanation of the steep upper edge as an artifact produced by self-absorption. In the first place most experiments were performed under a set of experimental conditions that served to reduce self-absorption. We used relatively low-energy (2 kV) and obliquely incident (45°) electrons and monitored x-rays emitted normal to the surface. As mentioned previously, a few measurements of the edge were made with extremely low excitation energies (1 kV) and oblique electron trajectories (~75° from normal) that would further reduce any self-absorption, but no differences in the edge shape were found. The second, and more important evidence against an important role for self-absorption, is contained in the emission curves themselves. The emission edge broadens rapidly as the temperature is increased and all other experimental parameters are held constant. Similar broadening has been observed in absorption.[12] If self-absorption produced the steep edge, it should persist at higher temperatures, since the overlap between the emission and absorption spectra is even greater at high temperature than at low temperature. In this respect, it is important to remember that a broader edge in the absorption coefficient at higher temperatures will not result in a significantly broader self-absorption feature in the emission spectra because the intensity is attenuated as an exponential function of the absorption coefficient and not as a linear function of that coefficient.

We also note that the strong temperature dependence of the broadening function provides an excellent explanation of the rounded edges observed for Li in experiments using emission cathodes operated above room temperature.[5] As is evident in Fig. 4, such curves appear to have an asymmetrically broadened edge with a (10–90)% width of about 0.7 eV, while the low-temperature data (Fig. 3) clearly resolve the high-energy shoulder.

Another possible explanation of the peak at about 54 eV in the emission data is that it represents a peak in the transition density of states. All calculations agree that a peak does appear in the conduction band density of states, but it is almost always assigned a position just above the Fermi level and thus should appear as a feature in the absorption spectra.[8] Such a peak has been observed at the expected position in the photoyield

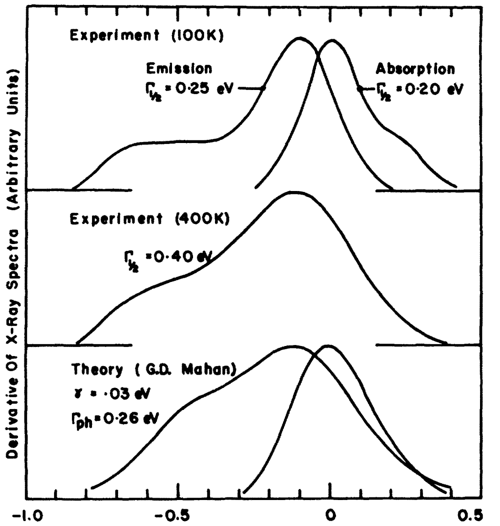

FIG. 7. Experimental curves are derivatives of x-ray spectra displayed in Figs. 4 and 6. Theoretical curves are derivatives of step function emission and absorption thresholds calculated by Mahan. They are reported from Ref. 10. $\gamma$ is a measure of the lifetime broadening of the core-hole level and $\Gamma_{\text{ph}}$ is the FWHM phonon broadening of the core-hole level assumed by Mahan for his calculations.

data of Peterson[13] and is presumably responsible for the peaking in the absorption data in Fig. 6 at a position some 0.3 or 0.4 eV above the absorption edge.

By far the most satisfactory explanation of the shape of the emission spectra is given by the recent theories of Almbladh and Mahan. They calculated the emission and absorption spectra when the relaxation time of the lattice is comparable with the lifetime of the core hole. A comparison of our results with the predictions of theory is given in Fig. 7. The experimental curves are the derivatives of the edge spectra given in Fig. 6 (emission and absorption at 100 K) and Fig. 4 (emission at 400 K). The bottom curves represent the theoretical absorption and emission intensities for a single electronic transition. They are not strictly comparable with the experimental curves since they represent the derivatives of phonon-broadened simple step functions rather than the true density of states. However, the effect on the spectra of the slowly varying density of states should not significantly change the more prominent features of the edge spectra. All curves are drawn relative to a zero chosen at the point of maximum slope of the absorption edge. We believe that the shoulder on the experimental absorption curve in Fig. 7 is due to a peak in the density of states.[8,12] The other features of the curves will be compared with theory.

In the Mahan-Almbladh theory, the critical parameter is $\gamma$, the broadening associated with the lifetime of the core hole due to Auger recombination. We compare our data with the calculations of Mahan since we have available to us a more complete account of his calculations. In Mahan's calculations when the hole lifetime is very short ($\gamma \gtrsim 0.05$ eV) recombination occurs before lattice relaxation, and an emission edge is observed with the point of maximum slope separated by 0.1 eV from the absorption edge. For long lifetimes ($\gamma \lesssim 0.01$ eV), the lattice relaxes before emission and the edges have a Franck-Condon shift to a point 0.5 eV away from the absorption edge. At intermediate lifetimes ($0.01 < \gamma < 0.05$ eV), the derivative spectrum of the emission edge is a double-peaked structure. An example is shown in Fig. 7 for $\gamma = 0.03$ eV. This structure can be qualitatively viewed as a superposition of two peaks, one at −0.1 eV, attributable to emission occurring before lattice relaxation, and another at −0.5 eV, attributable to emission after relaxation.

Excellent agreement is obtained between experiment and theory for the 0.1-eV separation between the peaks of the derivative spectra of the absorption and emission edges. This small edge separation is a persistent feature of the calculations for a wide range of $\lambda$ values. Mahan suggests that it is a small remaining Franck-Condon shift.[10] It is probably not an ordinary Franck-Condon shift, however, since it occurs in the calculations even for very short core-hole lifetimes.

Both experimental and theoretical derivative curves of the emission spectra show a double-peaked shape but the separation between peak structures is somewhat wider in the experimental curves (~0.5 eV) than in the theoretical curves (~0.4 eV). This implies that the Franck-Condon shift of the fully relaxed lattice is slightly larger than calculated by Mahan, but the difference is well within the range of uncertainties in his calculations and in the recent calculations of other theorists.[18,19] We judge from an examination of the published theoretical curves that the experimental edge shape is compatible with Mahan's values of $\gamma$ in the range of $\gamma = 0.030 \pm 0.005$ eV. A good fit to our data has been obtained by Almbladh using a value of 0.016 eV for $\gamma$.[20] Either theory places very close tolerances on the core-hole lifetime relative to the lattice relaxation time. The uncertainty of the absolute hole lifetime is somewhat greater, however, since it depends on the detailed treatment of the phonon dispersion in the calculations. These values of $\gamma$ fall well within the error limits assigned by Baer, Citrin, and Wertheim in their analysis of x-ray photoemission data. They find $\gamma = 0.020 \pm 0.015$ eV.[14] Glick and Hagen have recently calculated a value for $\gamma$ of about the same magnitude.[21]

Many broadening processes affect the x-ray edges. Of these, phonon broadening of the Fermi level is of the order of $2kT$ and therefore is very small. We have seen above that the lifetime broadening of the core hole $\Gamma_{1s}$ (FWHM) $= 2\gamma \simeq 0.06$ eV is also much smaller than the observed width of 0.20 to 0.40 eV. Yue and Doniach, in attempting to explain the very broad edges observed at high temperature in Li, suggested that many-body effects accounted for much of the edge broadening.[22] Our high-resolution low-temperature data and its interpretation in terms of the partial-relaxation theory makes it possible to explain the emission edge shape without invoking a significant many-body broadening. Thus, this interpretation of the emission data is consistent with recent interpretations of x-ray absorption,[12-14] x-ray photoemission,[14] and inelastic scattering data,[11,23] all of which indicate that many-body effects do not contribute in a significant way to the rounding of the Li $K$ edge.

Since the core hole lifetime and many-body effects do not contribute significantly to the observed width of the $K$ edge, the only remaining broadening mechanism is the phonon broadening of the core hole. Consequently we believe that the edge width $\Gamma_{\frac{1}{2}}$ indicated on the experimental spectra and plotted versus temperature in Fig. 5 is a reasonably good measure of the phonon effects after a correction has been made for the resolution of spectrometers. From Fig. 5 we see that the FWHM broadening corrected for instrument resolution ranges from $0.22 \pm 0.05$ eV at 85 K to about 0.38 ± 0.05 eV at 400 K. These values are in excellent agreement with the values of $\Gamma_{\mathrm{ph}}$ found by Baer, Citrin, and Wertheim in their interpretation of x-ray photoemission, x-ray absorption, and inelastic electron-scattering data.[14] An interesting feature of the calculations is that the total width, including phonon broadening, of the emission edge is always greater than that of the absorption edge. Mahan[10] suggests this may be due to phonon damping. This feature of the theory is consistent with our 100-K data where we observe a FWHM total Gaussian broadening of 0.25 eV in emission and about 0.20 in absorption. If we follow Mahan's theory and assign a 40% greater phonon-induced width to the emission edges than to absorption edges, we would conclude that the appropriate values of phonon broadening in lithium are approximately $\Gamma_{\mathrm{ph}} \simeq \Gamma_{1/2}/1.4 = 0.16 \pm 0.03$ eV at 85 K and $0.27 \pm 0.03$ eV at 400 K. These values are comparable in magnitude but somewhat smaller than the values found by Baer, Citrin, and Wertheim[14] in their analysis of other experimental data. The theoretical values of $\Gamma_{\mathrm{ph}}$ calculated by Hedin and Rosengren,[18] and Flynn,[19] although uncertain by a factor of 2, are consistent with the present results.

We conclude that an essentially complete and consistent description of the Li emission and absorption edges is now possible which includes the following features: (i) many-body effects are small and probably completely negligible, (ii) thermal broadening of the $1s$ core level via hole-phonon interactions dominates the broadening of the edges, (iii) the peak above the absorption edge is attributable to a density-of-states peak in the conduction band, and (iv) the peak below the emission edge is produced by the partial relaxation mechanism described by Almbladh and Mahan.

*Note added in proof.* R. S. Crisp has recently published the results of a study of the effects of self-absorption on the x-ray emission edges of Li and other metals [Philos. Mag. 36, 609 (1977)]. His results confirm our conclusion that self-absorption does not play a significant role in determining the edge shape of Li. C. O. Almbladh has recently published a full account of his partial relaxation theory [Phys. Rev. B (to be published)]. In recent measurements on Na, we have observed an excess width of the emission edge and a gap between the emission and absorption edges that indicate an important role for partial relaxation processes in explaining x-ray edge shapes in this material.

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* Permanent address: Physics Dept., University of Tennessee, Knoxville, Tenn. 37916.

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