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Temperature Dependence of the *K* X-Ray Emission Edge of Li†

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The *K* x-ray emission spectrum of Li has been measured with 0.1-eV resolution for temperatures between 85 and 490 K. A prominent shoulder is observed on the emission edge that is strongly broadened and shifted in energy as the temperature is raised. The peak in the emission spectrum lies about 0.6 eV below this shoulder. The steep high-energy edge of the spectrum is interpreted as a Fermi edge centered at 54.8 eV and having a width of 0.2 eV. The results are compared with similar structure observed in the absorption spectrum of Li.

The interpretation of the *K* x-ray edge of Li has long been a source of controversy. Both the soft x-ray emission (SXE)[1-6] and soft x-ray absorption (SXA)[7-9] edges have been measured by several workers. In emission data, there has been conflicting evidence as to whether the true emission spectra shows a steep high-energy edge with a peak at lower energies[1,4,6] or a gradual fall over about 0.8 eV from the peak of the emission spectrum.[2,3,5] It has been suggested that the steep edge is an experimental artifact which results from self-absorption.[10] This implies that the entire region above the peak in energy may be a very broad emission edge. On this assumption several theoretical attempts have been made to account for this very broad edge in terms of many-body effects[11-15] and lattice vibrations,[16-18] but the calculations have usually shown that the processes considered give much smaller edge broadening.

Considerable light was thrown on the Li edge problem recently by the measurements of Petersen and co-workers[7-9] who measured the SXA edge at temperatures from 4 K to above the melting point of Li (> 450 K) with good resolution (0.11 eV). At low temperatures they find a clear shoulder in the absorption edge.[7,9] They interpret the steeply rising region below the shoulder as the true Fermi edge. Their temperature studies indicate that the broadening (~ 0.2 eV at 80 K) of this edge is due predominantly to processes involving lattice vibrations.[8,9] A similar conclusion was reached by Baer, Citrin, and Wertheim[19] in their analysis of x-ray photoemission results. Following a suggestion by McAlister[10] which was based on an augmented-plane-wave (APW) band structure calculation, Petersen and Kunz attribute the peak above the shoulder to a peak in the one electron transition density located about 0.5 eV above the Fermi edge.

We have performed complementary experiments to those of Petersen and Kunz, measuring the soft x-ray emission spectra of Li with a resolution of 0.1 eV at a number of temperatures between 85 and 490 K. Our results are nearly a mirror image of theirs. A shoulder is present on the SXE edge at low temperatures that is broadened and shifted in energy by phonon processes as the temperature is raised. A peak is found about 0.7 eV below the Fermi edge. Our results show that the steep high-energy edge is not an artifact due to self-absorption, but represents the true Fermi edge. They also demonstrate that many of the differences in previous data can be attributed to differences in the temperature of the emitting cathode; the sharp edge observed at low temperatures[1,6] is washed out at higher temperatures. The results are important because they should serve to concentrate theoretical interest on the origin of the peak in the emission spectrum rather than on the breadth of its upper edge. To date no single band-structure calculation predicts a transition-density peak for both SXE and SXA data. In addition, the low temperature, high resolution, and careful energy calibrations used for the measurements allow us to give a more reliable estimate of the relative positions of the absorption and emission edges and thus to throw some light on the question of whether an energy gap exists between them.

The measurements were made on thick Li films (~ 10 000 Å) evaporated on a polished Cu block in an ion-pumped ultrahigh-vacuum chamber. The block was cooled by circulating liquid and heated by electron bombardment. Its temperature was monitored by a thermocouple clamped under a screw on the face of the block. The system operated at a base pressure of 2×10^{-9} Torr after a mild bakeout and at 1×10^{-8} Torr when connected to the monochromator used in the experiments. Pressure bursts to $\sim2\times10^{-7}$ Torr were observed during evaporation of the Li films. In five hours of measurements following evaporation, the intensity of the emission peak decreased about 25% until the sample was heated above the Li melting point at which time an additional drop of about 25% was observed. After storage in a 10^{-8}-Torr vacuum for six days, the Li peak level decreased to 35% of its original value and a LiO peak was observed with a magnitude 1/10 as large as the reduced Li peak. No significant change in the shape of the Li peak was observed as a function of time.

For the measurements reported here, the Li films were illuminated by a 3–4-mA beam of 2-kV electrons incident at an angle of 45° to the film surface. Soft x rays emitted normally from the sample surface were analyzed by a MacPherson 247 grazing-incidence monochromator equipped with a 1200-line/mm gold-coated grating and a Spiraltron detector. A careful calibration of the monochromator was made immediately before the experiment at a resolution of 0.07 eV using a spark spectrum of air which produces a multitude of sharp lines in the energy range of interest. The Li experiments were performed with slit widths of 50 μm and a resolution of 0.1 eV as determined directly from the half-widths of the line spectra at this slit setting. We believe that the energy scale is accurate to at least 0.03 eV.

To obtain high-resolution results, repeated spectral curves were digitized at approximately 0.025-eV intervals and added. Figure 1 shows the averaged results of fifteen measurements of the high-energy edge of the SXE spectra made at 85± 5 K shortly after a fresh evaporation of Li onto the liquid-nitrogen–cooled substrate. The most striking feature of the curve is the well developed shoulder at 54.7 eV. Assuming that the steep portion of the curve below the shoulder is the Fermi edge for emission, we can locate the edge at the center of the steeply rising portion of the curve (54.8 eV). The width of the edge is about 0.2 eV as measured between the 10 and 90% points of this initial rise. The maximum in the SXE spectra is located about 0.7 eV below this edge and a full 0.6 eV below the shoulder.

Figure 2 shows similar data for measurements at six temperatures between 85 and 490 K. The curve at 435 K gives data taken just below the melting point. Each curve represents averaged data from fifteen measurements. The curves are

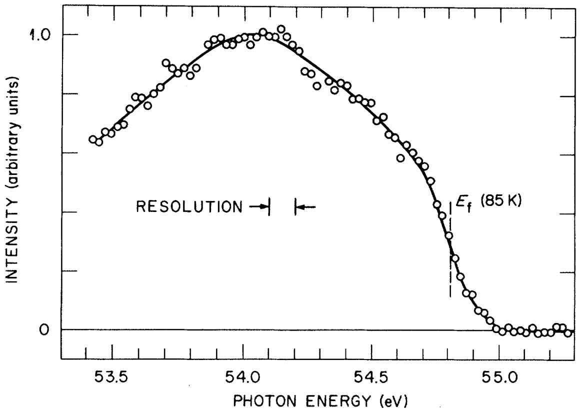

FIG. 1. The x-ray emission spectrum of Li at 85 K. The points are averages of fifteen measurements of the spectrum. The line is a smooth curve drawn through the points.

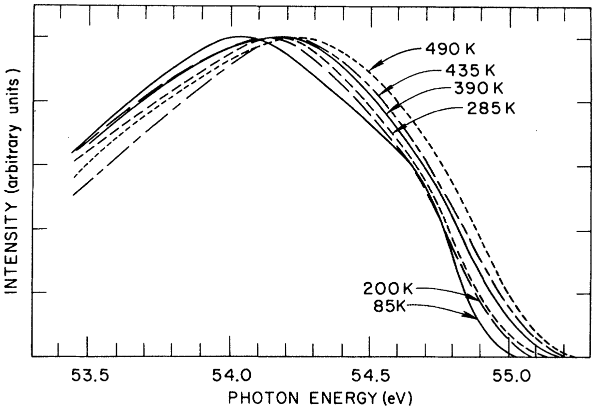

FIG. 2. Emission spectra of Li at six temperatures from 85 to 490 K. The curves represent smooth fits to digital data as in Fig. 1.

normalized to the same height. In a separate set of temperature cycling experiments, a reduction in peak amplitude of about 15% occurred between 200 and 440 K. This change was reversible so long as the sample did not melt. A further irreversible reduction of about 20% was observed when the sample melted. Clearly the curves are both shifted and broadened by the change in temperature. Again concentrating attention on the steep upper edge, we observe a shift of about 0.07 eV and an additional broadening of about 0.1 eV between 85 and 390 K. An additional shift of about 0.06 eV is observed between 395 and 490 K as the sample melts. The prominence of the shoulder is much reduced at 285 K and is no longer visible at 390 K except as a gradual change of slope.

In Fig. 3, we display two of our SXE curves along with the SXA curves of Petersen and Kunz. All curves are normalized to the same maximum height. The symmetry of the emission and absorption is quite striking. The steeply rising Fermi edges of both curves have about the same width. Moreover, both curves shift to higher energy and broaden by comparable amounts with changes of temperature. A separation of approximately 0.07 eV is observed between the Fermi edges of the SXE and SXA curves which is maintained as the curves shift and broaden with changes of temperature. This apparent gap between the edges should be viewed with caution, however, since the curves were made with separately calibrated instruments and calibration uncertainties are comparable in magnitude to the measured separation.

If we restrict our attention to the region near the Fermi cutoff, our results are in good agreement with theoretical results of Hedin and Rosengren[20] who calculated the broadening produced when tightly bound core electrons find themselves in a changing Coulomb potential due to the vibrations of the atoms of the crystal. If the Auger lifetime of the core hole is long compared to the relaxation time of the phonon distribution so that lifetime broadening of the SXE edge is small, then the same broadening function should mold both emission and absorption edges and there should be a Franck-Condon shift between them. The data of Fig. 3 are consistent with these assumptions and show a gap and edge width comparable to those that Hedin has calculated for lithium. Similar conclusions about the relative importance of phonon and lifetime broadening and comparable estimates of the broadening they produce has recently been extracted from an analysis of soft x-ray photoemission data by Baer, Citrin, and Wertheim.[19]

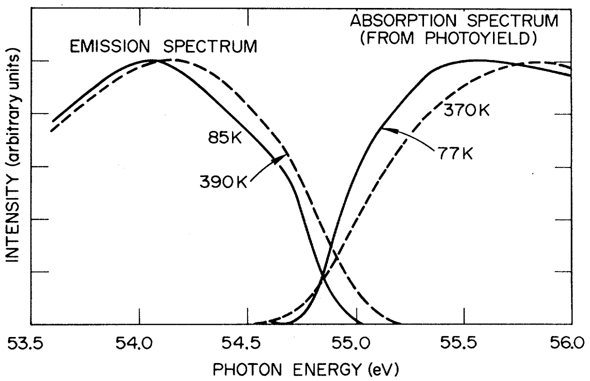

FIG. 3. Comparison of absorption and emission edges of Li. Absorption curves are taken from Ref. 7.

The major problem that remains is to account for the peaks in the SXE and SXA spectra that lie respectively 0.7 and 0.5 eV away from the Fermi edges. McAlister's APW calculations[10] and a model-potential calculation of Shaw and Smith[21] predict such a peak in the absorption spectra due to a peak in the one-electron transition density, but find no such peak in the emission spectra. Stott and March,[22] using a different formalism based on momentum eigenfunctions, find a transition density peak in the SXE spectra due to a peak in the transition probability, but do not consider the SXA problem. O'Keefe and Goddard[23] have suggested that a similar result could be obtained using spin-generalized rather than Hartree-Fock basis orbitals. We conclude that no combination of currently available one-electron calculations combined with various broadening processes can yet give a satisfactory account of both the SXE and SXA spectra of lithium, but that such an explanation may well be possible.

We conclude with a few comments on possible self-absorption effects. Our experiments were performed with excitation conditions that rough calculations indicate should give negligible self-absorption (2-keV electrons incident at 45° and normally emitted photons). Internal evidence in the data confirms the calculations. If self-absorption were important, the steep upper edge should persist to higher temperatures since emission and absorption probabilities do not change much with temperature and the overlap is greater at higher temperatures. Additional experimental checks were made by measuring the edge with excitations between 1 and 3 keV with the 45° gun, and by using a different gun which produced 1-keV electrons incident at 75° from the sample normal. In all cases the shape of the edge was unchanged from that observed with 2-keV electrons.

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Anomalous Conductivity of Quench-Condensed Sodium-Ammonia Films*

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Films of sodium and ammonia have been formed on substrates held at 5 K. The electrical resistivity of the films has been measured and a metal-nonmetal transition has been observed, but the transition was found to be anomalous in that the resistivity was not a monotonic function of the sodium concentration. No evidence was found for the anomalously high electrical conductivity reported for bulk sodium-ammonia solids which were quick-frozen from liquid solutions.

Recently, attention has been focused on the properties of quick-frozen sodium-ammonia solutions in which a transient high electrical conductivity was reported.[1,2] The results seemed to provide support for the thirty-year-old claim by Ogg[3] that sodium-ammonia solid solutions were superconducting and have resulted in a flurry of speculations relating to the existence of time-dependent superconductivity in such solutions.[4-7] Recent measurements,[8] however, indicate that this apparent transient conductivity is a result of the freezing process.

In an attempt to determine the intrinsic resistivity of sodium-ammonia solid mixtures, we measured the electrical resistivity of solid sodium-ammonia films formed directly from vapor onto substrates held at or below 5 K. The investigations, which were carried out as a function of sodium concentration, do not confirm the existence of high-conductivity states. The films do exhibit a metal-nonmetal (MNM) transition as a function of composition at concentrations in the 45–50 mole-percent-metal (MPM) range. The MNM transition is anomalous in that there appears to be what may be enhanced conductivity on the nonmetal side of the transition. The anomalous behavior may also be interpreted as a resistivity enhancement on the metallic side. Extreme-