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## Observation of the low-temperature martensitic transformation in Li and a Li–Mg alloy by soft x-ray emission

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**Abstract.** The martensitic transformation that occurs in pure Li metal and in alloys of Li with Mg has been well documented from the results of x-ray diffraction and electrical resistivity measurements.

We present here soft x-ray emission spectra from both bulk and evaporated samples of pure Li metal and of a Li + 10.7 at.% Mg alloy subjected to various cold-working and thermal treatments. We observe effects in the spectra from bulk samples of both pure Li and the alloy which we interpret as resulting from the transition; for samples prepared by evaporation of pure Li onto cooled substrates these effects are not observed.

### 1. Introduction

The alkali metals Na and Li and  $\alpha$ -solid solutions of Mg in Li undergo a martensitic transformation when cooled below liquid nitrogen temperatures in which the BCC metal transforms spontaneously to an FCC structure. This has been studied previously using x-ray diffraction methods by Barrett and Trautz (1948), Barrett and Clifton (1950) and Barrett (1956) and using electrical resistivity measurements by Dugdale and Guban (1961) and Oomi *et al* (1985, 1987). The latter authors demonstrated an enhancement of the resistance effects arising from the transition in Li–Mg alloys relative to pure Li metal.

The first authors claim the presence of an HCP phase for samples cold worked at room temperature and then cooled, whereas cold working at low temperatures after cooling produced only the FCC structure. This observation has been refuted by Overhauser (1984) using the neutron diffraction data of McCarthy *et al* (1980) which points to a single complex nine-layer rhombohedral structure (R9) at liquid helium temperature. The thermal details of the transition are given in the references (already) cited; for pure Li the onset of the transition occurs on cooling to about 75 K while reversion on warming commences at 95 K with completion by 150 K. For a 10.7 at. % Mg alloy, the composition used here, the onset and reversion temperatures are some 15 K higher.

Thermal expansion causes small but significant changes in the positions and profiles of the emission edges in the spectra of metals through changes in the lattice parameter, which scale the zone in  $k$ -space and in general lead also to a core level shift. The net effect is at least a shift in the emission edge to either higher or lower energies as reported

by Tagle *et al* (1980) for a number of metals and by Callcott and Arakawa (1977) who made a detailed study of thermal effects above liquid nitrogen temperature on the K emission edge of Li. Such shifts are seen in the temperature range down to liquid nitrogen temperature; below that temperature the thermal expansion for any metal is very small and will not give rise to significant effects in the spectrum. For Li, whose Debye temperature is 335 K, the thermal expansion in going from 80 K to 10 K is less than 0.1 of that in going from 300 K down to 80 K; thus effects seen in going from 80 K down to liquid helium temperatures should be attributed to other than the thermal expansion, in this case the phase transition. For Li K emission, as is seen in the present work, the effects of lattice expansion are manifested also as a shift of the peak.

Li metal has one conduction electron per atom; hence the Brillouin zone is only half filled and the energy contours are essentially spherical, although small distortions of the Fermi surface from a sphere are calculated (see, e.g., Ziman 1960). Because of the transition, it is not possible to observe the Fermi surface of Li directly via de Haas van Alphen or similar techniques, all of which require that the sample be held at liquid helium temperature. For the other alkali metals, precise DHVA measurements reported by Shoenberg (1969) indicate only very small deviations from a spherical Fermi surface. Thus the  $p$  density of states, which is seen reflected in the K emission spectrum, is to first order independent of the crystal structure and zone geometry, and changes arising from band-structure effects due to a phase change are not expected to be large. A further complication in studying the transition via the Li K spectrum is the anomalous profile of the high-energy portion of the spectrum which arises from the now well documented incomplete phonon relaxation effect (Almbladh 1977, Mahan 1977, Callcott *et al* 1977, Crisp 1977).

## 2. Experimental details

The spectra are dispersed by means of a 1 m radius concave grating ruled in gold with 2400 grooves  $\text{mm}^{-1}$  and a  $1^\circ$  blaze. The spectrometer operates in a scanning mode with the counts from the detector, an EMI 9642/2 electron multiplier sensitized by evaporating a 3000 Å layer of CsI onto the first dynode, being collected into a Digital Systems 11/23 computer. With entrance and analysing slits each set at 45  $\mu\text{m}$  the optical resolution is better than 0.25 Å in first order over the whole of the range from 13 to 265 Å covered by the spectrometer. This corresponds with 0.06 eV at 54 eV which is the peak of the Li K emission.

Spectra were excited by direct electron bombardment using a 2.0 kV beam focussed into an area approximately  $5 \times 0.5 \text{ mm}^2$ . 2.0 kV was chosen for the accelerating voltage as providing a good compromise between spectral intensity and self-absorption. No self-absorption correction has been performed on the data presented here and reference to the earlier experiments of Crisp (1983) show that at this accelerating voltage the correction is small. Beam currents of from 0.10 to 4.0 mA were used depending on permissible heat input for consequent temperature rise. Peak counts accumulated ranged from  $10^5$  for Li K spectra run at the higher temperatures to less than  $6 \times 10^3$  for the case of Mg  $L_{23}$  from the alloy at liquid helium temperatures.

The targets consisted of (i) bulk samples of pure Li metal, (ii) Li metal evaporated *in situ* in the target chamber onto a copper target as substrate and (iii) bulk samples of an alloy of Li with 10.7 at.% Mg.

The bulk Li samples and those of the alloy were scraped *in situ* with a tungsten carbide knife to prepare a clean surface and also to perform cold working. The ambient pressure was always below  $10^{-7}$  Torr during the scraping stage and in the range  $(2-5) \times 10^{-8}$  Torr when spectra were being recorded. There was no evidence of significant sample contamination by oxygen or nitrogen or by carbon or silicon from the cold-trapped Diffstack pumping system (Edwards CR 63). While recording spectra a second cold trap next to the target was cooled with liquid nitrogen.

The sample holder, which is the target or anode of the soft x-ray source, can be cooled with either flowing liquid helium or with liquid nitrogen or with cooled dry nitrogen gas to achieve sample working temperatures in the ranges 10–40 K, 80–110 K and 200–250 K. The actual temperature within the range depends on the electron beam power input to the target and is monitored by a thermocouple embedded in the sample. A simple calculation, backed up by experimental measurements, shows that the principal factor governing the working temperature in the emitting region of the sample is the thermal impedance between the back face of the sample and the target holder, to which the sample is clamped with a very thin film of silicone grease to improve thermal contact. The measured thermal impedance at this point was about  $12 \text{ K W}^{-1}$  for both bulk Li and alloy samples. The temperature rise due to heat flow through the bulk sample can be estimated; even though the target is not thermally shielded the radiation input is small and is negligible compared with the input from the electron beam. For the evaporated targets the sample temperature is very close to the substrate temperature. The target runs at the high voltage (2.0 kV); thus the millivoltmeter which indicates the thermocouple output is battery powered and floats electrically while the liquid helium or liquid nitrogen or cold gas cooling feeds are isolated by Teflon or polycarbonate insulating sections in the respective transfer lines.

In recording data at liquid helium temperatures the sample was scraped or evaporated and allowed to come to the lowest temperature before the beam was switched on. Thus the sample attains a temperature approaching 4.2 K, estimated at 6 K but certainly less than 10 K, at which the transformation is more or less complete. Because of the thermal hysteresis, reversion does not commence until 95 K or higher temperature is reached, and even if the sample temperature with the beam on is grossly underestimated the material will remain transformed.

Repeatable spectra were recorded from the following samples:

(i) Bulk samples of pure Li scraped to cut a fresh surface at 6 K, 80 K and 200 K (the scraper was precooled by contact with the back of the target holder prior to scraping; nonetheless it is considerably warmer than the sample when scraping takes place);

(ii) bulk samples of pure lithium, scraped at liquid nitrogen temperature (80 K) then warmed to room temperature and re-cooled to 6 K, 80 K or 200 K prior to recording the spectra;

(iii) pure lithium evaporated *in situ* onto copper substrates maintained at 6 K, 80 K and 200 K;

(iv) bulk samples of the alloy scraped at 6 K, 80 K and 200 K—ingots of the alloy, from which the targets were cut, were prepared by the method of Henry and Cordiano (1934) and are from the batch used by Crisp (1982).

### 3. Results and discussion

#### 3.1. Bulk Li targets

A typical series of spectra recorded from bulk Li samples scraped at several temperatures is illustrated in figure 1(a) and (b). The effects arising from the variation in temperature

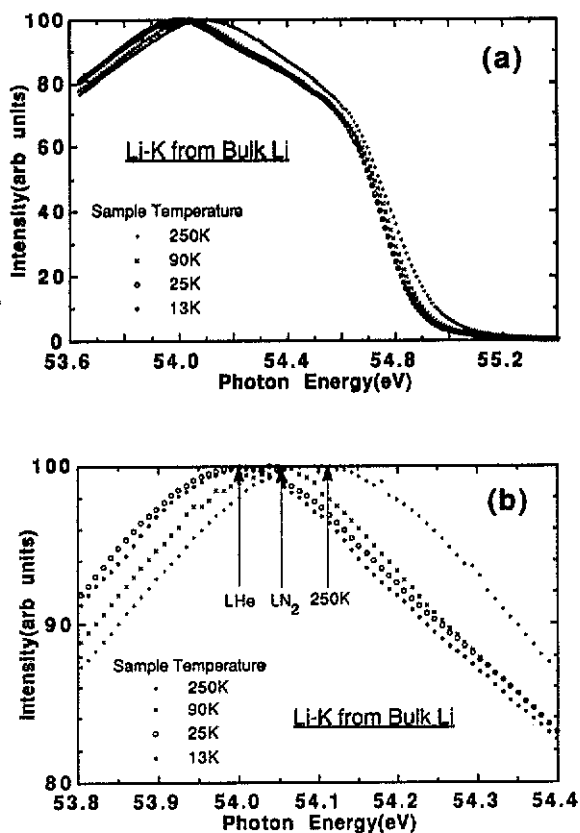


Figure 1. Li K emission from scraped bulk samples of Li metal at the temperatures indicated. (a) Peak and high energy portion of the band. (b) The same data on an expanded scale to show the peak shifts.

are small but reproducible for runs on different samples. Changing the temperature produces a shift in the high-energy portion of the band, evident from a shift in the position of the maximum, and a slight straightening of the portion immediately above the peak in energy. The low-energy portion is unaltered. The emission edge, i.e. the portion of the spectrum above about 54.6 eV, is predictably sharpened in going to lower temperatures. In going from 250 K to 90 K the peak shifts  $0.050 \pm 0.015$  eV to lower energies; in going to 10 K a further shift of  $0.040 \pm 0.015$  eV is observed.

For bulk Li targets that were scraped at liquid nitrogen temperature, warmed to room temperature and then recooled to liquid nitrogen or liquid helium temperature, similar spectra are observed. Since the Debye temperature of Li is 335 K, little annealing is expected to take place at 300 K; thus these samples are cooled through the transition temperature in a cold-worked state and apparently behave in the same way as samples that are scraped (i.e. cold worked) below the transition temperature. It was not possible to scrape at room temperature in the present set of experiments; thus we have not exactly duplicated the conditions used by Barrett and Trautz (1948) under which the HCP phase is reputed to be favoured.

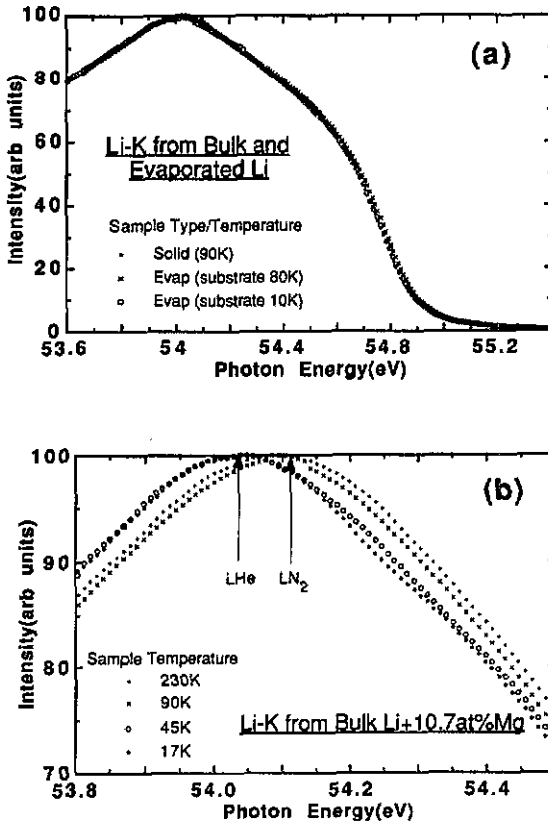


Figure 2. (a) Peak of the Li K emission from bulk Li scraped at 90 K and from Li evaporated to substrates held at 80 K and 10 K. (b) Peak of the Li K emission from the Li + 10.7 at.% Mg alloy scraped at the temperatures indicated.

### 3.2. Evaporated targets

Figure 2(a) compares spectra from bulk targets at 90 K with those from targets where Li is evaporated to substrates at 80 K and 6 K. For the evaporated targets there is no difference (within experimental error) from bulk Li scraped at 90 K.

### 3.3. Bulk Li-10.7 at.% Mg alloy

The Li K spectrum from the alloy behaves similarly to that from the pure metal when scraped (cold worked) at liquid helium temperatures in that the peak is seen to shift  $0.055 \pm 0.015$  eV from its position at 90 K. The marginally larger shift is at least consistent with the larger effect seen for the alloy in electrical resistivity measurements by Oomi *et al* (1985).

The Mg L<sub>23</sub> band cannot be recorded in its entirety due to the long-wavelength limit of the spectrometer falling at  $263 \text{ \AA}$  (47.2 eV) which is in the middle of the band. The edge region is accessible, however, and in figure 3 it is seen shifted and very much broadened with respect to the pure metal which is shown for comparison in the figure. The broadening, combined with the relatively low intensity and the background due to

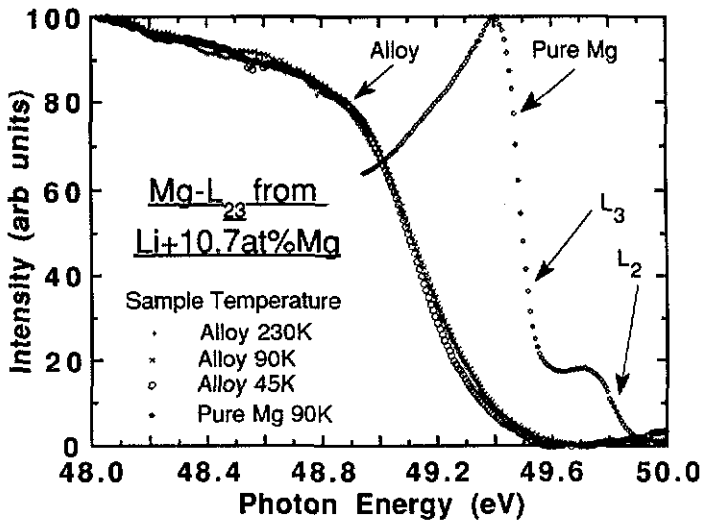


Figure 3. The  $L_{23}$  emission edge of Mg in the Li + 10.7 at.%Mg alloy at three temperatures showing the large broadening in the alloy and no evidence of the phase transition. The  $L_{23}$  emission edge from pure Mg metal at 90 K is included for reference to show the shift and broadening in the alloy.

the underlying tail of the Li K spectrum, obscures the  $L_2$ - $L_3$  separation which is clearly evident for the pure metal. There seems to be no detectable effect, within experimental error (which is considerably larger than for the Li K spectrum), of cooling to liquid helium temperatures.

### 3.4. Discussion

For monovalent Li, where there is only a small distortion of the filled energy contours due to proximity with the zone boundary, we do not expect phase changes to cause dramatic first-order changes in the emission spectrum. However, changes in lattice parameter, which scale  $k$ -space, should be similarly reflected in the emission spectrum from the filled states. Thus in going from 300 K to 90 K Herbstein and Averbach (1956) find that in bulk Li the lattice parameter decreases by  $0.027 \text{ \AA}$  (or 0.8%) and in the present experiments this is seen in the observed 0.05 eV shift in the peak. The further 0.04 eV shift in going to 25 K, which is of the same order of magnitude, then must be due to a structural rearrangement since thermal expansion, estimated at  $<0.003 \text{ \AA}$ , would not produce an effect of this magnitude. (A simple calculation using a Debye model and a Debye temperature of 335 K shows that the thermal expansion from 90 K to 10 K is about 0.09 times that from 300 K to 90 K. Thermal expansion or structural rearrangement in a phase change will both be seen in band-structure changes and in core-level energy shifts and are manifested here as shifts to lower energies of the peak of the Li K emission.)

As is evident from figure 2(a), a bulk sample scraped at 80 K or samples evaporated onto substrates at 80 K or 6 K all yielded identical Li K spectra. We conclude that there is no structural difference, apart from that due to thermal expansion, between

evaporated Li deposited at liquid nitrogen or liquid helium temperature and bulk material at higher temperatures, and that all three forms have the same BCC structure.

The shape of the high-energy portion of the Li K band, with the 'premature' peak of 54 eV lying some 0.75 eV below the true emission edge, depends on the special relation in the case of Li between the phonon relaxation time and the lifetime of core holes for radiative decay, leading to incomplete phonon relaxation and a modification of the emission profile. This has been discussed fully by Almladh (1977) and Mahan (1977) and related to the soft x-ray emission and absorption edges by Callcott *et al* (1977) and Crisp (1977). Since the premature peak in the profile is unchanged at the lowest temperatures, this special relation is apparently preserved even after the structural transformation. (In fact, the experimental spectra suggest that the effect may even be slightly accentuated in transformed Li.) There are no data for the Debye temperature or elastic constants for the R9 rhombohedral form of Li to compare with those for the BCC phase; from the spectra we must assume these are similar to those in the BCC form. Alternatively, we might conclude that the incomplete phonon relaxation mechanism is *not* responsible for the effects seen both in emission and absorption, and especially the crucial calculated and measured separation of the emission and absorption edges by 0.1 eV. This contention would not be easy to sustain in the face of all the evidence.

For the Li K spectrum in the alloy, the effect of the transition, as judged by the peak shift, is marginally greater than for the pure metal. The Mg L<sub>23</sub> spectrum for the alloy is seen grossly broadened compared with that for pure Mg and shows no effects due to the transition. Such broadening is expected and commonly observed in the solute spectrum from a random solid solution. Similarly the edge shift, due to a core-level shift for the solute atom in the solvent crystal environment, is commonly seen, and has been noted before in the Li-Mg system by Crisp (1981, 1982). Notwithstanding that the vicinity of the Mg sites is expected to have  $e/a > 1$  due to screening the divalent cores and thus be more sensitive than the vicinity of Li to any structure changes, a combination of factors reduces the sensitivity experimentally of the Mg L<sub>23</sub> emission in the alloy to the effects of any phase change. For the 10.7 at. % concentration of Mg in the alloy the intrinsic intensity of Mg L<sub>23</sub> emission is low and the band sits on a relatively high background from the tail of the Li K band which gives an  $(S - B)/B$  ratio of 4.0. These factors combine with the random alloy solute broadening to smear the experimentally observed spectrum. Given the relatively poor statistics, attempts to recover detail by numerically unfolding the broadening do not succeed.

It is hoped that this work might stimulate a theoretical band-structure calculation for Li atoms in the R9 structure as well as a calculation or measurement of the parameters of the phonon relaxation and its effect on the profile of the emission spectrum. It is also worth commenting that an experiment involving such a transformation is of particular interest in investigating the extent to which the crystal environment influences the x-ray emission profile through band structure effects compared to the extent to which the profile depends on the local field in the cell of the emitting atom. It seems, from the data presented here, that the latter dominates in Li and the principal effect of structural changes is seen as a core-level shift.

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was reawakened by correspondence with Professor S B Woods of the University of Alberta which stimulated the present improved series of measurements.

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