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Neutron scattering investigation of pressure-induced phase transitions in Li and Ba

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Abstract

The elemental alkali metals as well as the earth-alkaline metal barium undergo phase transitions from an ambient bcc structure to close-packed structures (fcc or hcp, respectively) in a largely varying pressure range from 4.5 GPa in Cs up to more than 50 GPa in Na. Little is known about the mechanisms of these pressure-induced phase transitions. In particular, it is an open question whether the bcc \rightarrow fcc and bcc \rightarrow hcp transformations are related to similar phase transitions at ambient pressure and low temperatures which occur in Li and Na but are absent in the heavy alkali metals and in Ba. In the present work, we have adapted the Paris–Edinburgh pressure cell for neutron scattering studies on single crystals of Li and Ba. It was found that under carefully chosen experimental conditions almost hydrostatic loading of Li and Ba up to about 7 GPa is possible. We describe the experimental methods which have allowed us to overcome the technical difficulties and report the first results of elastic neutron scattering on Li and Ba and inelastic neutron scattering on Li.

1. Introduction

The alkali metal lithium shows a phase transition from bcc to fcc at 7.5 GPa [1]. The alkaline-earth metal barium transforms from bcc to hcp at 5.5 GPa [2]. The *structures* of these high-pressure phases and the sequences of further phases at even higher pressures up to 100 GPa have been clarified by powder diffraction techniques during the past few years (e.g. [3] for Li, [4] for Ba) while, by way of contrast, very little is known about the *mechanisms* of these transformations [5].

On the other hand, extensive investigations were performed on the reconstructive phase transitions from bcc to close-packed structures which are observed in Li and Na at ambient pressure and low temperatures. Lithium exhibits a rather complicated low-temperature phase diagram with the coexistence of several phases and a large thermal hysteresis [6]. On cooling below 80 K, a closed-packed 9R-phase (stacking sequence ABCBCACAB) and a disordered polytype are formed. On heating, the 9R-phase transforms to fcc and above 120 K the original

bcc single crystal is recovered. During heating to room temperature recrystallization takes place in the re-transformed single crystal, leading to its decomposition into a polycrystal. The equilibrium phase is probably fcc. However, direct nucleation of fcc from bcc is prevented due to the large lattice misfit between these two phases which is nearly absent between 9R and bcc [6–8]. The low-temperature martensitic transformation in Li is related to an inherent instability of the bcc lattice under $[110][\bar{1}10]$ shear distortions, resulting in a soft shear modulus $c' = (c_{11} - c_{12})/2$ and a low-lying acoustic $TA_1[110][\bar{1}10]$ phonon branch. A moderate but clearly anomalous softening of this branch has been observed as a precursor effect over a wide temperature range upon approaching the transformation [9].

Temperature-induced transitions are absent in the heavy alkali metals and in Ba. Nevertheless, similar mechanisms to those governing the transformations in Li and Na at ambient pressure have been suggested for the pressure-induced phase transitions. If this is indeed the case this should be reflected by pertinent precursor phenomena, namely corresponding changes of the phonon frequencies as a function of pressure and the occurrence of elastic diffuse scattering. Alternatively, it has also been proposed that the transformations have their origin in pressure-induced changes of the electronic band structure [10], i.e. a mechanism of entirely different nature which would not give rise to the mentioned precursor effects. Motivated by this situation, an investigation of the lattice dynamics and the elastic diffuse scattering on approaching the transition from below and, if possible, also from above appears desirable.

Such experiments require the use of single crystals. Neutron studies covering the pressure range in question were performed in the past using the well-known Paris–Edinburgh cell [11] (figure 1(a)) including successful investigations of single-crystalline Fe, Zn and Ge up to more than 10 GPa. An extension to the case of alkali and earth-alkaline metals, however, is not straightforward. As a result of the extreme softness of these materials, an elaborate loading technique is needed, permitting the application of hydrostatic pressure without severe plastic deformation of the single crystals. In addition, the high chemical reactivity of the samples necessitates assembling the pressure cell in a glove box under protective gas. Accordingly, various modifications in the design and handling of the pressure cell were required. These are described in the present work together with the first results of elastic and inelastic neutron scattering on Li and Ba single crystals under conditions of almost hydrostatic loading up to about 7 GPa.

2. Modifications of the standard setup of the Paris–Edinburgh pressure cell

The Paris–Edinburgh pressure cell was initially developed to increase the pressure range accessible to neutron diffraction studies up to 10 GPa or even higher values. In the initial setup its design is based on a portable hydraulic press of about 50 kg with a loading capacity of up to 200 tons. The pressure can be changed *in situ*. Two opposed anvils made of tungsten carbide compress the sample which is surrounded by a gasket. The shape of the gasket (two toroidal rings) allows a horizontal confinement of the sample by corresponding grooves machined into the anvils.

Four tied rods leave space for horizontal opening angles of about 4×70 degrees for the incoming and scattered beam. Problems with the use of standard pressure-transmitting liquids like mixtures of methanol and ethanol, pentane and isopentane or pure methanol and the need for hydrostatic compression led a group at ISIS to design a slightly different anvil profile and gasket arrangement for powder samples [12]: above 2 GPa anvil failure by radial cracking, presumably caused by progressive propagation of microcracks in the anvil material, required a construction excluding any direct contact of the pressure-transmitting liquid with the anvils.

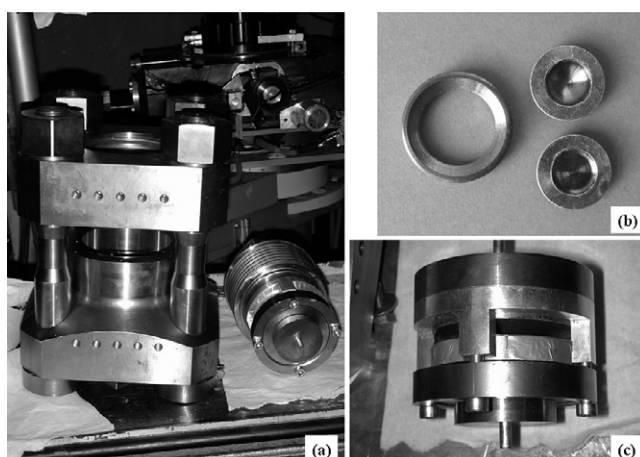


Figure 1. The Paris–Edinburgh pressure cell with the disassembled inner support at the right-hand side (a), CuBe caps and the gasket (b), and the inner support which allows one to apply an initial pressure by screwing in order to keep the system tight (c).

In this setup the powder is placed into two flanged hemispherical caps which replace the inner ring but leave the overall dimensions of the gasket unchanged.

In working with single crystals one has to take into account that a deviation of only a few degrees from a given vertical orientation of the sample would already give rise to a substantial loss of the scattered intensity due to absorption in the anvils (due to strength restrictions of the anvil material the vertical aperture is less than $\pm 7^\circ$). Therefore, we modified the geometry of the lower hemispherical cap in such a way as to obtain a flat inner surface (figure 1(b)), keeping the sample orientation well-defined and allowing for a rather precise alignment of the sample inside the caps.

Due to the softness and high chemical reactivity of elemental Li and Ba the choice of an appropriate pressure-transmitting medium was essential. We note that, in contrast to earlier investigations, soft metals like lead cannot be used since both Li and Ba are much softer than lead. The selection of a fluid is severely restricted by conflicting requirements: chemical compatibility with the reactive samples, an acceptable high-pressure behaviour and absence of hydrogen in order to avoid incoherent scattering. After careful tests a mixture of deuterated octane–decane was chosen for lithium and Fluorinert for barium. The hemispherical caps were machined of copper–beryllium and their contacting surfaces were electrolytically tinned in order to keep the system tight. The corresponding gasket was also machined out of copper–beryllium.

3. Experimental details

Cylindrically shaped crystal rods of high-purity ^7Li and Ba were grown using the Bridgman technique [13]. The vertical accessible angle of less than $\pm 7^\circ$ for the incoming and the scattered beam requires a good collimation as well as a precise knowledge of the orientation of the samples. Therefore, the orientation of the rods has to be determined with high precision prior to the cutting of the samples. For Li this could be achieved by x-ray Laue techniques but for Ba only neutrons can be used. Subsequently, platelets of about 4–5 mm diameter and 1 mm thickness were cut by spark erosion. All Li samples were single crystals whereas the Ba sample consisted of three crystal variants.

The samples were mounted into the caps in a glove box filled with an inert gas, e.g. He. To avoid formation of gas bubbles during the assembling procedure both the sample and the caps were immersed in a bowl filled with the pressure-transmitting liquid (an additional complication arises from the buoyancy of Li due to its low density of 0.53 g cm^{-3}). Afterwards the caps were fixed between the pressure stamps and an initial pressure of about 1 kbar was applied by screwing together the pressure stamps with a specially designed support (figure 1(c)). This initial pressure is necessary to prevent leaking of the system while mounting it into the pressure cell at the spectrometer. It has to be mentioned that all these initial steps have to be performed inside the glove box.

Elastic diffuse neutron measurements up to 6.8 GPa for Li and 3.8 GPa for Ba as well as phonon measurements up to 3.9 GPa for Li were done at the Orphée reactor of the Laboratoire Léon Brillouin (LLB) in Saclay, France, on the cold three-axis spectrometers 4F2 and G43, respectively. Decreasing intensities at higher pressures and limitations of the allocated beamtime prohibited measurements at higher pressures. The spectrometer G43 VALSE is situated at a cold neutron guide in the guide hall whereas the spectrometer 4F2 is located in the reactor hall. Both spectrometers were operated using a pyrolytic graphite monochromator and analyser. At G43 the monochromator is vertically bent and the analyser is flat. 4F2 has a double monochromator. A wavelength of 0.236 nm was chosen and, in order to avoid contaminations from second-order contributions, a pyrolytic graphite filter was inserted in the incoming beam. All inelastic measurements were done at the spectrometer 4F2 in down-scattering mode (phonon creation).

The uncertainty of the vertical orientation of the sample is about $\pm 5^\circ$, which is due to (i) misalignment of the oriented crystals before cutting ($\pm 1^\circ$), (ii) the cutting of the platelike samples from the cylindrically shaped single crystals ($\pm 1^\circ$) and (iii) the floating of the sample in the transmitting liquid ($\pm 3^\circ$ or even more).

Due to the mounting procedure and the impossibility of fixing the sample position inside the caps it is not possible to define the orientation of the crystal within the horizontal plane beforehand. To avoid possible shading of Bragg reflections due to the fourfold symmetry of the pressure cell a (111) scattering plane was chosen where six (110) Bragg peaks can be found. If the vertical alignment is within the limits of the opening angle of the pressure cell it is guaranteed to find two (110) reflections needed to determine the sample orientation.

The beamtimes required for the experiments were rather long due to several boundary conditions leading inevitably to low scattering intensities:

- ^7Li has an exceptionally small coherent scattering cross section $\sigma_c \sim 0.62$ barn;
- Ba has an exceptionally low Debye temperature $\Theta_D \sim 110$ K entailing a strong intensity decrease due to the Debye–Waller factor;
- the sample volume is restricted to $\sim 10 \text{ mm}^3$ inside the hemispherical caps;
- a good horizontal collimation of the beam is necessary in order to avoid spurious contributions from various parts of the pressure cell which lowers the available flux further.

Measuring times for each data point varied from 2 min (determination of the lattice parameter) up to 44 min (phonons at 2.4 and 3.9 GPa). Differences between G43 and 4F2 resulted from the considerably lower neutron flux at G43 and the tighter collimations used.

For higher pressures difficulties arose from the Debye–Scherrer lines of the gasket and the caps. Because the variation of the lattice parameter of the sample with pressure is different from the variation of the lattice parameter of the much harder material of the caps and the gasket, the Debye–Scherrer lines of the sample environment are not restricted to those regions of the scattering plane where they are observed at ambient pressure. Instead, their position relative to the reciprocal lattice of the sample crystal changes as a function of pressure, thereby

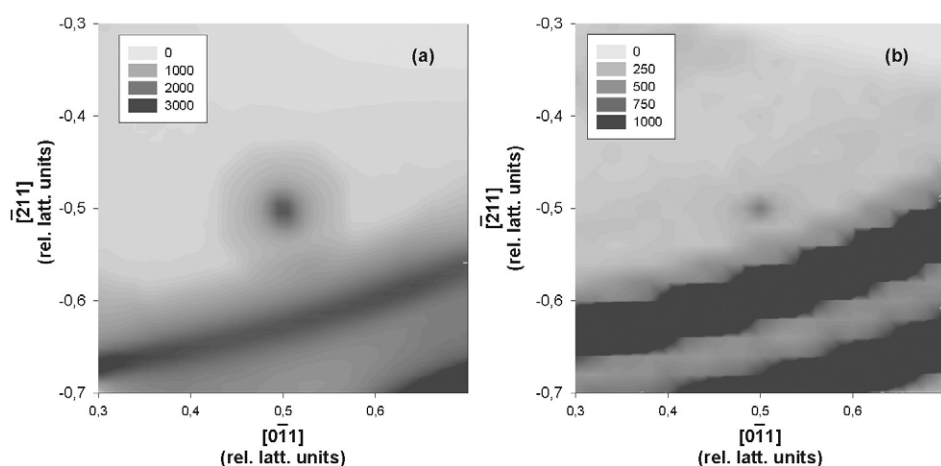


Figure 2. $(1\bar{1}0)$ peak of Li at 0.3 GPa (a) and at 2.4 GPa (b). In this (111) scattering plane (defined by the two perpendicular directions $[0\bar{1}1]$ and $[\bar{2}11]$) the $(1\bar{1}0)$ peak has the coordinates $(1/2^*[0\bar{1}1], -1/2^*[\bar{2}11])$. The dark lines below the Bragg peaks belong to the Debye–Scherrer lines of the CuBe caps. In (b) the Bragg position lies closer to the rings and the Bragg intensity has decreased.

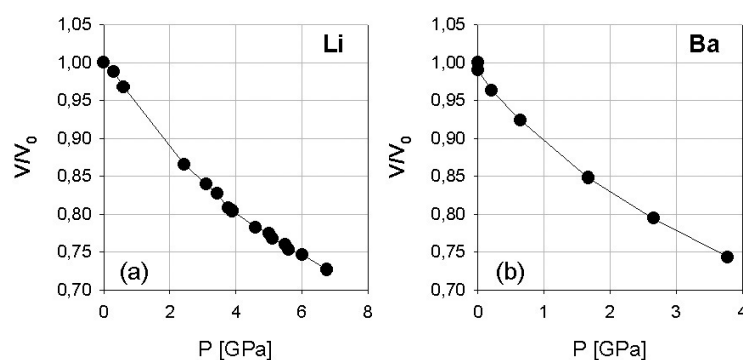


Figure 3. The pressure–volume dependence for Li (a) and Ba (b). V_0 denotes the cell volume V at ambient pressure. Error bars do not exceed the symbol size.

approaching and ultimately shadowing certain Bragg reflections (cf figures 2(a), (b)). This is difficult to avoid, even when choosing a different material for the caps and the gasket, since the volume change of Li and Ba amounts to $\sim 30\%$ within the pressure region of interest.

4. Results

Figure 3 shows the volume decrease of Li and Ba, respectively. The values of the unit cell volume V are derived from lattice parameter measurements at the (011) Bragg peak. Pressure calibration was done by comparing the resulting volumes with synchrotron x-ray data (see [14] for lithium and [15] for barium). The full width at half maximum (FWHM) of the (011) Bragg reflection in Li changed from 0.8° at ambient pressure to 3.1° at 6.8 GPa and in Ba from 1.9° at ambient pressure to nearly 10° at 3.8 GPa.

During a measurement at G43 one of the Li samples transformed from bcc to fcc already at a constant pressure of 5.5 GPa (i.e. well below the expected transition pressure of 7.5 GPa)

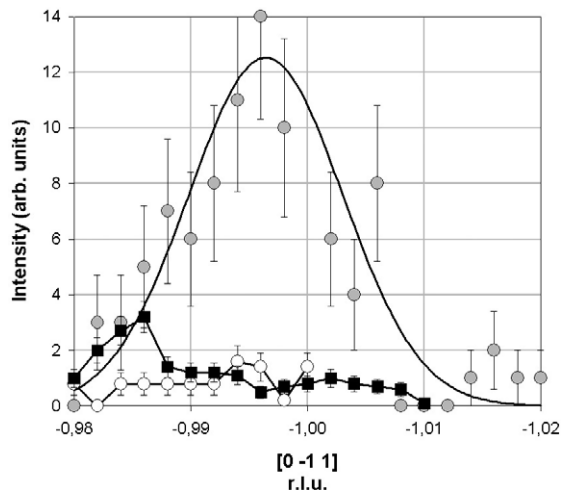


Figure 4. Radial scans over the bcc (011) peak in Li at 5.5 GPa. The first fast scan (grey circles) was done immediately after the application of pressure. A second scan (black squares) with better statistics was started later; however, the Bragg intensity vanished after several data points and did not reappear (white circles). The disappearance of the peak occurred about 90 min after application of pressure.

after an incubation time of about 90 min (figure 4): after a first fast scan to roughly determine the lattice parameter (1 min per point; grey circles) the intensity vanished while scanning a second time with much better statistics (10 min per point; black squares). In another sample no indication of a phase transition was observed up to 6.8 GPa at 4F2.

These observations are reminiscent of former investigations of the low-temperature transformation in Li [13, 16] where, occasionally, the phase transition was found to occur up to 10 K above the transition temperature $T_c \sim 80$ K after different incubation times ranging from 2 min to 5 h, thereby demonstrating a strong dependence of the kinetics on the temperature history of the samples. The present results suggest that the pressure-induced bcc \rightarrow fcc transformation depends, similarly to the low-temperature transition, on the history of the sample with respect to the thermodynamical variables.

No hardening of the $TA_1[\zeta\zeta 0][\bar{1}10]$, $\zeta = 0.4$ phonon was observed with increasing pressure (figure 5) in contrast to the usual stiffening of the interatomic potential upon decrease of the lattice parameter. Possibly, the expected hardening is compensated by a softening due to the inherent instability of the bcc lattice on approaching the phase transition. Again, this would establish a connection with the phase transformation at low temperature and ambient pressure where a softening of this branch was observed upon cooling [9].

5. Conclusions

Both the observed incubation character of the phase transition in Li as well as the unchanged phonon frequency up to 3.9 GPa indicate a similarity of the underlying mechanisms governing the pressure-induced and the temperature-induced transitions. Further investigations of the phonon dispersion relations as well as the search for possible elastic precursors are necessary for a deeper understanding of the pressure-induced phase transitions in Li and Ba.

Although it has been shown that both elastic and inelastic measurements are possible in Li and Ba under high pressure, further efforts are needed to shorten the required measuring times.

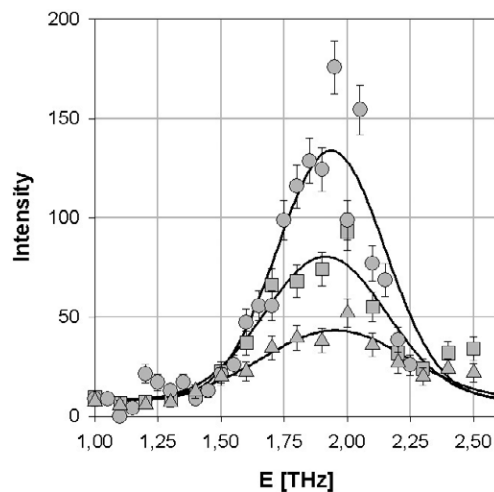


Figure 5. The $TA_1[\zeta\zeta 0][\bar{1}10]$ phonon in Li for $\zeta = 0.4$ at 0.3 GPa (circles), 2.4 GPa (squares) and 3.9 GPa (triangles). Intensities are normalized to the incoming neutron flux. Lines represent Gaussian fits to the data. Gradual broadening of the mosaic width of the crystal and additional shading of the sample volume by the pressure stamps lead to the observed diminution of the intensity with pressure.

These include evacuated collimation tubes before and after the sample to minimize background contributions from the pressure cell and from air scattering, the use of the zero-scattering alloy $Ti_{66}Zr_{34}$ for the hemispherical caps and the gasket as well as the design of a pressure cell for larger samples.

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