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Small-angle neutron scattering of alkali metals at moderate uniaxial pressure and low temperature

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Abstract

This paper reports on the development of a cryostat for neutron small-angle scattering experiments on alkali metals under uniaxial compression in a temperature range from 5 K to room temperature. The investigation was motivated by earlier observations of 'premartensitic' anomalies in metallic lithium and potassium which seem to suggest that nuclei of a low-temperature phase might be generated in the undercooled bcc structure either by cooling alone or by additional mechanical deformation. Cooling to 120 K in lithium and to 5 K in potassium, respectively, without applied load produced only very slight changes in the SANS patterns. However, after uniaxial compression of 3% at these temperatures anisotropic scattering patterns developed, suggesting the formation of small particles embedded in the bcc matrix whose orientation is related to the deformation direction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Pure lithium undergoes a partial martensitic transformation at 80 K on cooling. The low-temperature phase consists mainly of a rhombohedral 9R structure, but contains a significant amount of a one-dimensionally disordered polytype phase of random stacking. The transformation is incomplete down to the lowest investigated temperatures, the volume content of the bcc matrix amounting typically to ∼90% at 80 K and ∼10% at 5 K. On heating from low temperatures, above 100 K the 9R and the disordered polytype phase transform into a perfect fcc structure. This rearrangement of the stacking sequence does not affect the bcc matrix. Subsequently, a gradual fcc → bcc transformation in the range from 120 to 180 K restores the original bcc single crystal, though with an increased mosaic spread [1–3].

Within the temperature range of the undercooled bcc phase, i.e. 80 K $\leqslant T \leqslant$ 180 K, virgin lithium single crystals exhibit a number of physical anomalies, in particular a pronounced enhancement of self-diffusion [4], a moderate phonon softening of the low-energy $TA_1[110][\bar{1}10]$ phonon branch [2], and an anomalous behaviour of the critical resolved shear stress in uniaxial tension and compression [5, 6] which cannot be explained by intrinsic

dislocation mechanisms in the bcc phase. The diffusion anomaly has been attributed to fluctuations (dynamic embryos) of the low-temperature phase. Similarly, the mechanical anomaly can be well understood if one assumes that small static nuclei are formed under the influence of a uniaxial deformation and subsequently interact with the glide dislocations. Taking into account the fact that the 9R phase is unstable above 100 K, such nuclei are expected to be of fcc type. Recent experimental and theoretical work [7, 8] strongly indicate that the true low-temperature equilibrium phase of lithium is fcc, whereas the 9R phase is metastable, helping to bypass an unsurmountable nucleation barrier from bcc to fcc.

Potassium, in contrast to lithium, does not undergo a macroscopic-scale phase transformation down to the lowest temperatures investigated (about 1 K). However, a softening of several per cent of the entire $TA_1[110][\bar{1}10]$ phonon branch below 100 K (not a soft mode!) and increasing elastic diffuse scattering with decreasing temperature close to Bragg reflections have been interpreted as precursors of a lattice instability [9]. Recent *ab initio* calculations by the present authors (to be published) have indeed shown that the fcc as well as the 9R zero-temperature ground state energy is lower than that of bcc; thus, two phase transitions at low temperatures are to be expected. Actually, the nucleation and growth of these phases might be blocked as a result of the bcc-specific immobility of dislocations at such low temperatures [10, 11]. In this case it seems possible to induce a phase transition, at least in the nucleation stage, by a mechanical deformation.

2. Experimental details

Due to the experimental requirements and the extraordinary properties of lithium and potassium (such as mechanical softness and high chemical reactivity) an appropriate treatment method and a special cryostat for low-temperature neutron investigations under uniaxial stress were developed.

The cryostat, shown schematically in figure 1, is based on a commercial closed-cycle cooling system (Sumitomo RDK-408D 4 K cold head and CSW-71D compressor) providing 31 W refrigeration capacity at the first stage (18 in figure 1) and 1.0 W at the second stage (17), at 4.2 K. The cryostat is evacuated by a conventional turbomolecular drag pumping station to a vacuum $\leqslant 10^{-3}$ Pa ($\leqslant 10^{-5}$ mbar).

A container (4) for liquid nitrogen (LN_2) with a capacity sufficient for several hours was placed below the blind flange at the top of the cryostat. Although temperatures down to 10 K can be reached within 2 h without liquid nitrogen precooling, the use of it speeds up the cooling considerably and, more importantly, permits 5 K to be reached even under stress when the compression rod is in contact with the sample. A thermal shield (16) surrounding the cold head, the sample holder and the LN_2 container was designed in order to suppress the heat transfer by radiation which is of importance below 25 K. Since no load in tension was intended to be applied, and because of the advantage of the outstanding features of quartz, namely the very low thermal conductivity and the relatively high strength in compression, the compression rod (5) was made of a quartz tube to reduce the heat flux.

Temperature is measured by a four-lead silicon diode (8) placed close to the sample (9). Suitable thermal contact is ensured by the use of Apiezon® N grease. Since the cooling compressor is constructed only for continuous work, the temperature is regulated by a computer-controlled heating system. Below 150 K it ensures an accuracy of ± 2 mK by temperature regulation 18 times per second through a programmable power supply unit that powers a Thermocoax heating coil (10) soldered into the copper plate directly beneath the sample chamber. The plate is suspended on four long thin-walled tubes (6) (wall thickness 0.5 mm) of high-strength stainless steel welded to the bottom of the liquid nitrogen container.

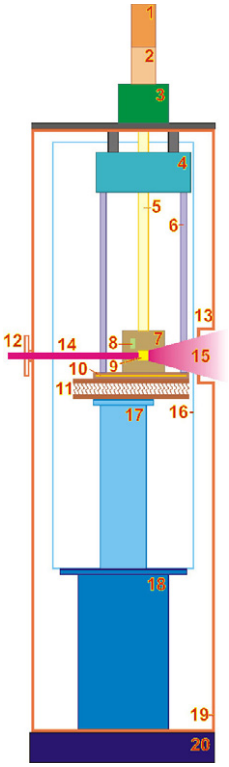

Figure 1. Schematic diagram of the deformation cryostat. 1—motor, 2—gears, 3—force transducer, 4— LN_2 container, 5—quartz compression rod, 6—four stainless steel tubes, 7—removable internal sample chamber, 8—silicon diode, 9—sample, 10—Thermocoax heating coil, 11—copper wires, 12—incident beam fused silica window, 13—100 mm × 100 mm square window, 14—incident beam, 15—diffracted radiation, 16—thermal radiation shield, 17—second and 18—first stage of the cold head, 19—cryostat external wall, 20—cryostat base.

The deformation unit of the cryostat allows for a maximum load of 1 kN and for uniaxial compression at constant deformation velocities between 0.05 mm min^{-1} and 10 mm min^{-1}. The cross head stroke amounts to 7 mm with a precision of 5 μm. The drive motor (1) with its gears (2) and the load transducer (3) are placed outside the vacuum chamber in order to operate at normal pressure and at room temperature. This is important especially for the load transducer because of its temperature-sensitive measuring method. Load, displacement and temperature are recorded by a GPIB-based data acquisition system and especially developed software.

The main challenge in designing the equipment was the high chemical reactivity of the materials to be investigated. Since the preparation of samples cannot be carried out in air, and since the heavy cryostat is far too large for handling under protective gas, a small internal sample chamber was designed (7). It stays mechanically decoupled from the very frail cold head, but thermally connected to it by a brush of minute copper wires (11). Furthermore, the sample chamber can be easily removed from the cryostat and channeled into a glove-box, where the samples are chemically polished in a bath of pure diethylketone in order to remove oxidation layers. They are then washed in petroleum benzine and finally mounted into the sample chamber. After sealing the openings for the neutron beam and for the compression rod with thin aluminium foil, the sample chamber can be transferred and finally assembled

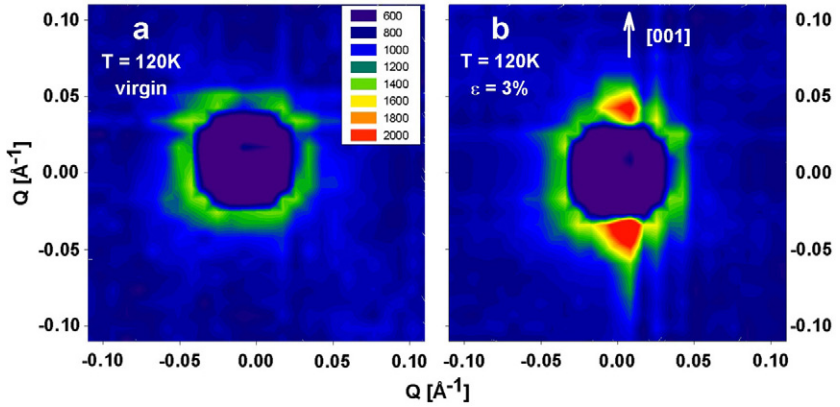

Figure 2. SANS patterns of Li: (a) virgin crystal at 120 K, (b) after 3% uniaxial compression at 120 K. The shaded area in the centre is masked by the beamstop.

into the cryostat. During the transfer the sample remains in the gas-tight chamber protected from oxygen and water vapour. At the beginning of the deformation experiment, when the cryostat is already evacuated, the compression rod perforates the aluminium foil. The cryostat is provided with a fused silica window of 15 mm diameter for the incident neutron or x-ray beam (12) and, on the opposite side, a square window of 100 mm × 100 mm size for the diffracted radiation (13). The sample–detector distance can be as small as 50 mm.

This design and the appropriate handling technique guarantee avoiding any surface oxidation of the samples during their lifetime.

The investigated samples were single crystals of high-purity potassium and of the pure isotope ^{7}Li, grown by the method of combined vacuum distillation and Bridgman growth in one vessel (described in detail in [6]). The crystals were oriented using the x-ray Laue transmission method and cut by spark erosion into cylinders of 10 mm diameter and 10 mm length, with the cylinder axis of the sample parallel to a [001] direction which was also the compression direction in the SANS measurements.

The SANS measurements were performed on the spectrometer PAXE at the Laboratoire Léon Brillouin, Saclay, France. Incident neutron wavelengths were 0.47 nm for Li, and 0.48–2.0 nm for K. The sample aperture was set to 7 mm diameter, which was much narrower than the sample size, in order to avoid any scattering from parts of the sample chamber or from the compression rod. This was verified by reference measurements of the empty cryostat. In order to reach adequate counting statistics, measuring times from 2 to 18 h were chosen for each of the successive steps. In order to avoid any surface oxidation of the samples that might produce a signature in the SANS pattern which, even in the high vacuum of the cryostat, could not be completely excluded during such long measuring times at ambient temperature, the first scans of the virgin Li and K crystals were performed at 250 and 70 K, respectively. According to our experience, these temperatures, although sufficiently high to be used as reference points, are at the same time low enough for the alkali metals not to react with oxygen and water vapour so that the samples remain metallically clean over many hours.

3. Results

Figure 2(a) shows the SANS pattern of lithium after cooling to 120 K in which the reference scan at 250 K has already been subtracted. There is a very slight increase in the scattered intensity, concentrated in an isotropic ring at $Q \sim 0.03$ Å^{-1}. Application of a uniaxial compression of

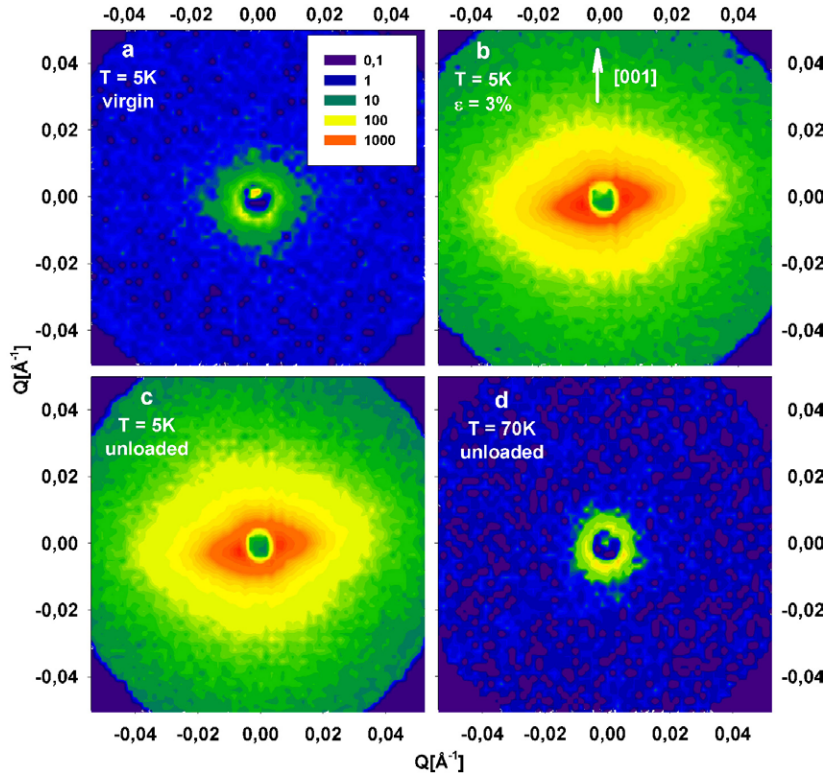

Figure 3. SANS patterns of K at a wavelength of 0.8 nm: (a) virgin crystal at 5 K, (b) after 3% uniaxial compression at 5 K, (c) after unloading at 5 K, (d) reheated to 70 K (for further explanation see text).

3% at 120 K (figure 2(b)) drastically changed the scattering pattern. A pronounced intensity increase appeared along the [001] loading direction, pointing to the formation of particles elongated in the (001) plane perpendicular to the compression direction. In three further scans, first at the same temperature after unloading, subsequently after heating to 250 K and finally after a further cooling to 100 K, the scattering pattern introduced by the deformation at 120 K persisted and showed very little change. Additional 3% compression at 100 K, however, again yielded a pronounced increase in intensity though the qualitative appearance of the intensity distribution did not change significantly.

SANS patterns of potassium, measured at a wavelength of 0.8 nm, are shown in figure 3. The background pattern was determined at 70 K. Subsequent measurements at 10, 7.5 and 5 K (figure 3(a)) did not exhibit noticeable changes. Application of a uniaxial compression of 3% along [001] at 5 K induced strong additional scattering which, however, in contrast to lithium, extended in the direction perpendicular to the deformation axis (figure 3(b)). No significant changes were observed after unloading at the same temperature (figure 3(c)). However, after heating to 70 K the scattering intensity caused by the compression at 5 K disappeared completely, with only the background remaining (figure 3(d)).

4. Conclusion

The present SANS investigations provide evidence for the formation of nuclei of low-temperature phases in lithium and potassium induced by uniaxial compression along [001]

at 120 and 5 K, respectively. The different orientations of the anisotropic scattering patterns can be understood by taking into account that the structure of the nuclei is very likely fcc in Li at temperatures above 100 K while our preliminary *ab initio* studies indicate that they are 9R in potassium. An estimation of the particle size from plots of the scattering intensity as a function of the transferred momentum yields a lower limit of ∼10 nm for Li. For potassium, where measurements at several different wavelengths are available, the size of the nuclei ranges from ∼10 up to and possibly beyond ∼100 nm. The visibility of the nuclei in the SANS experiment derives from the volume change associated with the phase transition ($\Delta V/V$ is of the order of some 10^{-3}) which is in reasonable agreement with the observed scattering intensities.

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