Experimental evidence for lattice instability of potassium at low temperatures

O. Blaschko
Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

M. de Podesta
H. H. Wills Physics Laboratory, University of Bristol, Bristol B58 1TL, United Kingdom

L. Pintschovius
Institut für Nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe, Postfach 3640, D-7500 Karlsruhe, Federal Republic of Germany

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Experimental evidence is presented for a tendency towards a lattice instability in potassium at low temperatures by neutron scattering techniques. The main result is the observation of a Huang diffuse scattering below 70 K in the vicinity of the (110) and (220) bcc Bragg reflections. Furthermore, the transverse-acoustic-phonon branch in the [110] direction with polarization [110] shows a softening of a few percent between 100 and 4 K, similar to Na and Li.

The lattice instability of the bcc structure in sodium and lithium was investigated recently by neutron scattering techniques revealing a softening of the low-lying transverse-acoustic TA[110][110] phonon branch, especially for zone-boundary phonons.[1-3] The softening favors a phase-transition mechanism occurring by microscopic shears on every second (110) bcc plane, leading to stacking faults within the bcc matrix.[1] Moreover, a diffuse scattering unmodulated in reciprocal space was observed, showing a thermal hysteresis connected with the formation of the new phase. This diffuse scattering was ascribed to defect formation as precursor phenomenon to the incipient structural change.[1,2] Evidence for a defect structure was further corroborated by the finding of a Huang-type diffuse scattering at the high-Q size of the (110) bcc reflection in lithium. In addition, a series of investigations on the low-temperature phase of Li and a further recent confirmation of the previous results have shown that Li has a faulted $9R$ structure below the martensitic transition.[4,5,6,3]

On the other hand, potassium, where despite its similarity to Na and Li no phase transition was known to occur, was taken as a sample for the search for charge-density waves in alkali metals. Low-temperature anomalies in rather macroscopic quantities as, e.g., in specific heat, were explained as signatures of charge-density waves.[7]

First indications for the results presented in the following were found during a recent search for charge-density waves in K.[8] It was noticed that at low temperatures the mosaic width of the K crystals increased. This observation initiated the present neutron scattering investigation dealing once more with low-temperature structural properties of potassium. It yields the first convincing evidence for a tendency towards a lattice instability in potassium at low temperatures.

The experiments were performed on two triple-axis spectrometers at the ORPHÉE reactor in Saclay. The spectrometer VALSE is located at a cold-neutron guide position. Incident-neutron wavelengths of $\lambda=2.35$ and 5.7 Å were used, with pyrolytic graphite and beryllium as filters. The overall collimations were 30′. The second spectrometer ($2T$) is located at the thermal source. The measurements on $2T$ were performed with collimations 15′, 15′, 20′, and 20′. Pyrolytic graphite PG (002) and PG (004) were used as monochromator and analyzer, respectively. Two single crystals of potassium with a size of about 10 cm^3 and a mosaic width of 30′ were used as samples.

In a first part of the experiment the soft transverse-acoustic-phonon branch in the [110] direction with polarization [1$\bar{1}$0] was investigated as a function of temperature (see Fig. 1). Between 200 and 100 K only small changes were observed. Upon further cooling to 5 K, this phonon branch shows a softening of a few percent

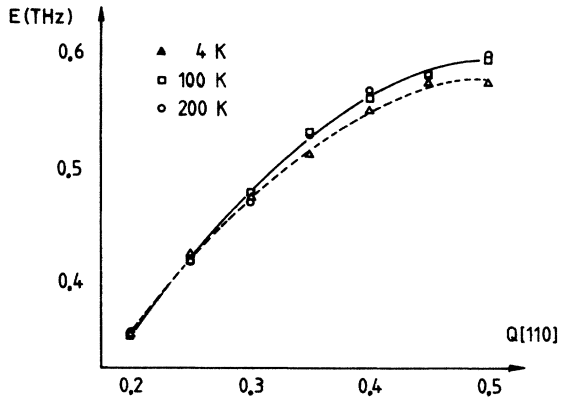

FIG. 1. The transverse-acoustic-phonon branch in the [110] direction with [1$\bar{1}$0] polarization at 4, 100, and 200 K, respectively (the solid line shows a sine function).

near the zone boundary, as found for Na and Li before.[1-3] The softening in potassium is similar in size to that observed in sodium, which undergoes a phase transition near 36 K, but is smaller than in lithium, where the phase transition occurs near 70 K.

In a second part of the experiment the diffuse scattering was investigated at different temperatures. During this investigation the sample was cycled between 200 and 4 K. For both crystals investigated, the mosaic structure always increased after some temperature cycles down to 4 K. The amount of the increase varied from cycle to cycle. Apparently it depends on the thermal history of the crystal. During these temperature cycles the diffuse scattering was explored especially in the vicinity of the (110) and (220) lattice reflections by radial scans through the reciprocal-lattice points. The scans revealed a Huang-type diffuse scattering at 4 K which decreased at high temperatures. In Fig. 2 the results of both (110) and (220) reflections are shown for three temperatures, when the crystal was heated up from 4 to 200 K. For both reflections the diffuse intensity is always higher at the high-Q side of the reciprocal-lattice point. After the first observation the diffuse scattering was reinvestigated with high resolution. The diffuse scattering reappeared, slowly increasing below 70 K and saturating at 25 K, but its intensity was lower than before and apparently depends on the thermal history. This is confirmed by an inspection of data obtained during the previous search for charge-density waves in another crystal: a Huang-type scattering also appeared in the second crystal at low temperatures, with similar characteristics as in Fig. 2(b), but a factor of 5 smaller in intensity.

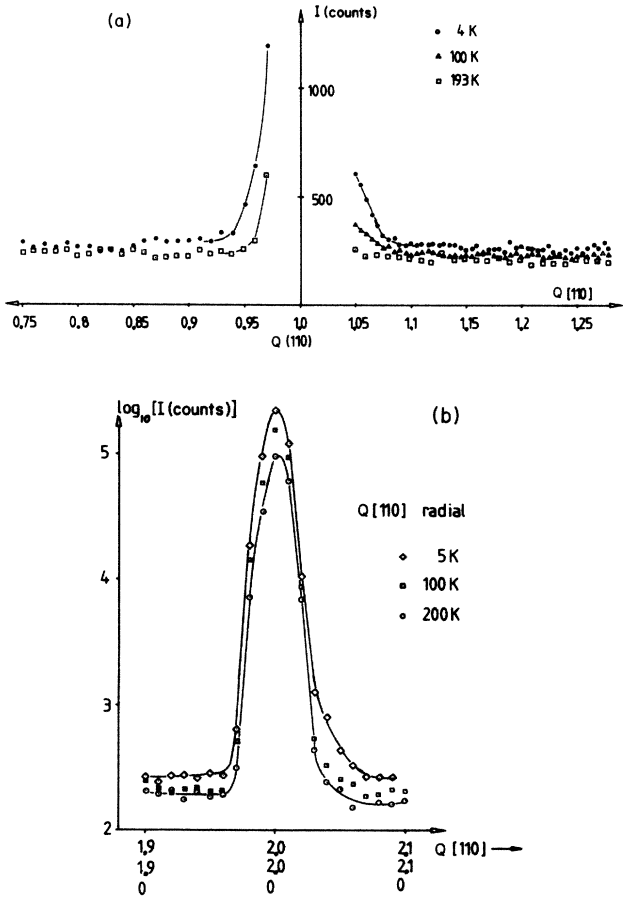

FIG. 2. (a) Neutron diffuse intensity in radial scans through the (110) bcc reciprocal-lattice point as a function of temperature when the crystal is heated up. (b) The same as in (a) on a logarithmic scale for the (220) bcc reflection.

The question may arise to whether the observed effects in K are experimental artifacts, due, in particular, to contamination from surface oxide layers.

First, the softening of the phonon branch is an intrinsical bulk property of K metal. Second, the diffuse scattering increasing at the bcc reciprocal-lattice points, i.e., (110) and (220), shows the periodicity of the bcc K lattice. This fact is further corroborated by scans perpendicular to, e.g., $(2+q\ 2+q\ 0)$ positions, showing that the diffuse scattering reflects the mosaic structure of the bcc matrix. It is therefore very unlikely that oxide layers with generally different structural characteristics are responsible for the Huang scattering observed. Moreover, it is not easily seen how the temperature dependence of the diffuse scattering, i.e., its appearance below 70 K and its disappearance at higher temperatures, can be correlated with the presence of surface oxides. Surface contaminations on potassium crystals such as oxides and hydroxides are easily visible already during their early stages of formation. Since the crystal looked completely metallic, surface layers, if there were any, must have been extremely thin. Therefore, spurious contributions to the scattering intensity due to oxide layers should be lower, by orders of magnitude, than the diffuse scattering observed, e.g., in Fig. 2(b).

Finally, we think that the irreversible changes in the mosaic structure are not induced by thermal stresses. The crystal was mounted on a sample holder whose thermal-expansion coefficient is much lower than that of potassium, and diaphragms were set so that the part of the crystal lying close to the holder would not be exposed to the neutron beam. However, we cannot entirely exclude the possibility that the changes of mosaic spread are due to thermal stresses. Nevertheless, we would like to emphasize that one argument does not depend on the mosaic structure (though its behavior goes well with our interpretation), but is based on the observed phonon softening and Huang scattering.

In view of these experimental results we conclude that the observed temperature-dependent intensities have the signature of Huang scattering produced by defect formation in potassium at low temperatures. Inelastic scattering contributions, which might be expected in the vicinity of Bragg reflections, should indeed decrease at low temperature. From the characteristic asymmetry of the diffuse intensity around the Bragg position it follows from more general arguments of Huang scattering theory that the defect structure created below 70 K is of interstitial type.[9] The first stages of the transition from the bcc to a hcp or 9R structure may consist of stacking faults on (110) bcc planes, in which only a few atoms are involved.[1] Stacking faults with finite size may be described as dislo-

cation loops creating the Huang scattering observed.

Moreover, the formation of the defect structure observed below 70 K and the subsequent distortion of the bcc matrix may explain the irreversible changes in the mosaic structure noticed during the whole experiment.

In the present work, we have shown that potassium shows a tendency towards a structural instability at low temperatures. The main evidence is given by the appearance of a Huang-type scattering. In reasonable agreement with an incipient phase transition in K is the zone-boundary softening of the TA[110][110] phonon branch at the zone boundary similar in size to that found recently in Na, where the bcc instability is a well-established fact.

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