

Comments

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Comment on "Structures of sodium metal"

O. Blaschko and G. Krexner

Institut für Experimentalphysik, Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

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Results of an investigation on the structures of sodium metal have been presented in a recent paper by R. Berliner, H. G. Smith, J. R. D. Copley, and J. Trivisonno [Phys. Rev. B **46**, 14 436 (1992)]. As one of the major conclusions of their work, Berliner *et al.* claim that there is no evidence of any precursor effects to the low-temperature phase transition in sodium as reported earlier by the present authors [O. Blaschko and G. Krexner, Phys. Rev. B **30**, 1667 (1984)]. We show that this statement is at variance both with available experimental data and pertinent theoretical work in the field.

In a recent paper¹ Berliner, Smith, Copley, and Trivisonno present results of an investigation on the structures of sodium at low temperatures. They report their findings to disprove earlier results of the present authors on the existence of precursor phenomena to the low-temperature phase transition in sodium. It is the purpose of the present comment to show that this is definitely not the case.

We start by citing a paragraph from the Introduction of Berliner's paper¹ which contains a correct summary of previous results of the present authors and thus leads directly to the topic under discussion.

"In the case of the alkali metals, this picture (i.e., the occurrence of precursor effects preparing the bcc-hcp phase transition) is controversial. Blaschko and Krexner² studied the diffuse scattering, phonon-dispersion curve and product phase crystallography for the martensitic transformation in sodium metal. They found a few percent softening of the $\Sigma_4[hh0]$ phonon branch in the region from $h \sim 0.3$ to the zone boundary, where reciprocal lattice vectors are defined in the usual manner: $Q = 2\pi(ha^* + kb^* + lc^*)$. This was in comparison to a slight hardening for the remainder of that branch and for the other phonon branches. In addition, they observed a temperature-dependent diffuse scattering above the martensitic transformation temperature, which was attributed to the formation of an intermediate defect structure. Similar effects were observed by Ernst *et al.*³ in lithium metal. These results are contradicted by other workers,⁴⁻⁷ who did not observe the phonon anomalies or the pretransition diffuse scattering other than spin-dependent diffuse scattering."

This passage inevitably leaves the reader with the impression that the work of the present authors regarding the $\Sigma_4[hh0]$ phonon branch and the diffuse scattering^{2,3}

is at variance with the results of four different experimental investigations.⁴⁻⁷ We, therefore, briefly examine the evidence contained in the cited papers before we go on to discuss the data presented by Berliner *et al.*¹

In Ref. 4 Dolling, Powell, and Martel investigated various phonon frequencies in sodium between 90 and about 40 K. However, with exception of one single phonon (at the zone boundary) they did not determine any frequency shifts of the $\Sigma_4[hh0]$ branch in question. In addition, since they were in search for a possible soft-mode behavior, they expected an effect exceeding the one presently under discussion by one order of magnitude. Therefore, the accuracy of their measurements was less than ours and also the temperature range investigated was limited. Nevertheless, we readily give their result for the single q value where a comparison can be made: at the zone boundary Dolling, Powell, and Martel⁴ found a softening of about 1% between 90 and about 40 K while in our work² we obtain a frequency decrease of about 3% between 230 and 40 K. So Dolling's shift observed over a temperature range of about 50° is in good agreement with our shift found over a range of 190°. Diffuse scattering has not been investigated by Dolling, Powell, and Martel.

The next reference cited by Berliner *et al.*⁵ reports phonon-dispersion relations for lithium at 98 K. Since no measurements at other temperatures have been performed it is impossible to derive any frequency shifts. Diffuse scattering has not been investigated.

The third reference⁶ is dealing with a diffraction experiment on poly-crystalline lithium under pressure. Neither the term "phonon" nor "diffuse scattering" are even mentioned in this work.

The fourth reference is an earlier paper of Stedman⁷ reporting on the phase transition in sodium. Phonon frequency shifts with temperature were investigated, howev-

er, did not cover the $\Sigma_4[hh0]$ branch which is the only one of interest in the present context. Likewise, no reference to diffuse scattering is made in this work.

To summarize, three out of four references purportedly contradicting our findings in sodium do not contain any information on the topics under question. The evidence of the fourth one, though limited, is in complete agreement with our results.

Regarding lithium—mentioned as well in the above-cited paragraph—we point to its similarity with sodium in many respects and observe that in a recent paper⁸ one of the authors of the paper we are commenting on has himself confirmed the phonon softening near the zone boundary reported by Ernst *et al.*³ We proceed now to examine the data presented in the paper by Berliner *et al.*¹

Berliner *et al.* studied the behavior of the zone-boundary phonon ($q=0.5$) in some detail. The results are given in Fig. 3 of their paper and show a softening of a few percent on cooling from 200 to 30 K. In discussing the significance of this effect Berliner *et al.* argue that the data at 30 K have to be omitted due to the fact that the specimen had already partially transformed. We do not believe that this indeed entails a noticeable change of the observed phonon frequency since the phonon obviously is well-defined and its width is even considerably smaller than the one observed just above the phase transition at 40 K. However, we adopt the reasoning of Berliner *et al.* and restrict the determination of the frequency shift to the range between 200 and 40 K thus obtaining a softening of about 3%. By comparison, our own measurements resulted in a decrease of about 3% between 230 and 45 K and about 4% between 230 and 14 K, respectively (see Fig. 1 of the present Comment). On the whole, concerning the zone-boundary behavior the data of Berliner *et al.* and the results obtained by the present authors are in good agreement and there is no contradiction.

In Fig. 2 of their paper Berliner *et al.* present measurements of the entire $\Sigma_4[hh0]$ phonon dispersion curve as determined at three different temperatures (295, 150, 40 K). Due to the low melting point of sodium the relevance of the shifts observed between 295 and 150 K is restricted so that the stated absence of any phonon softening is essentially based on two sets of measurements taken at 150 and 40 K. Since the accuracy of the data is not specified it is difficult to assess the significance of these measurements. However, regarding the error bars presented in Fig. 3 for $q=0.5$ as typical it is evident that the accuracy required to derive definite conclusions from a single temperature step has not been achieved.

By contrast, the earlier phonon-frequency measurements of the present authors² were performed at six different temperatures between 230 and 14 K. These earlier results (including error bars) are once again presented as Fig. 1 of the present article in order to facilitate further discussion. Though there is some scatter in the position of individual points a definite change in the behavior of the phonon-frequency shifts as a function of temperature is observed along this branch leading gradually from the usual hardening at low q values to an anomalous

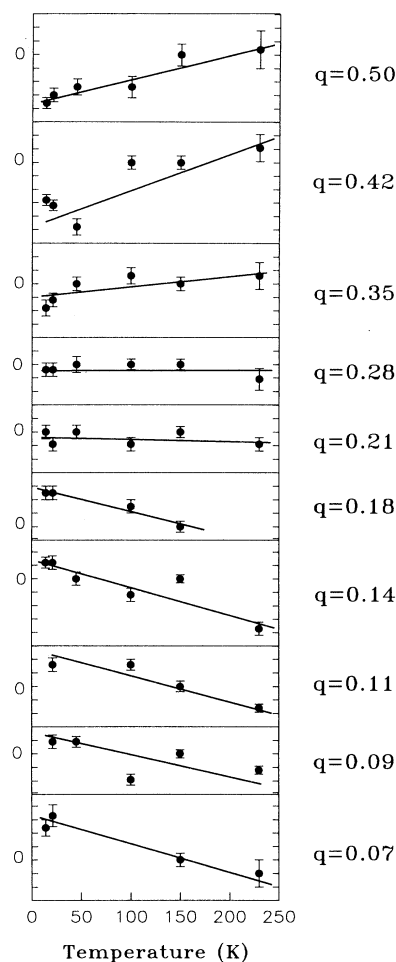


FIG. 1. Relative phonon-frequency shifts $\Delta\omega/\omega$ versus temperature for the $\Sigma_4[hh0]$ phonon branch in sodium (published in Ref. 2). One scale unit of the ordinate means 1%. As point of reference for the calculation of the phonon-frequency shifts, arbitrarily, the phonon frequency at 150 K was chosen corresponding, respectively, to zero on the ordinate. The lines have been drawn to guide the eye. Only a small fraction of the order of 1% of the sodium crystal used in this work did actually transform at low temperatures, so the phonon measurements performed below 36 K are characteristic of the high-temperature phase.

softening at large q values.

Berliner *et al.* report measurements of elastic diffuse scattering near the reciprocal lattice point (110) at 80 and at 40 K. They observe an intensity increase of about 7% at 40 K which is attributed to spin incoherent scattering whose temperature dependence is claimed to be in accordance with recent literature on the Debye-Waller factor of Na.^{9,10} Therefore, they reject the interpretation of earlier measurements of diffuse scattering by the present authors as being due to lattice defects associated with the phase transition. We agree that the intensity change between 80 and 40 K observed by Berliner *et al.* may result in part from the temperature dependence of spin-incoherent scattering, however, we note two important

additional features of the diffuse scattering which were reported by the present authors in their original paper.² First, the slope of the temperature dependence of the diffuse scattering exhibits a marked increase near 40 K (still well above the phase transition temperature). Secondly, the elastic diffuse scattering shows a strong hysteresis extending up to about 100 K on heating the sample. We do not know whether these features have been investigated by Berliner *et al.*, yet we emphasize that neither of them lends itself easily to an explanation based exclusively on spin-incoherent elastic scattering. Another passage of the paper of Berliner *et al.* we should like to comment upon is the following:

“However, anharmonic lattice dynamics calculations of Li, Na, K, Rb, and Cs all predict that the N'_4 low-lying mode should decrease with decreasing temperature. Many systems behave this way; Pb and Nb are examples. A low-lying zone-boundary mode in TaC, one of the highest melting compounds known, behaves similarly and it is not ready to transform. It is not correct, then, to say that this effect in the alkali metals is a precursor to the martensitic transformation.” (p. 14 438)

First, we observe that in earlier anharmonic lattice dynamical calculations for the alkali metals^{11–13} it is found without exception that it is precisely the $\sum_4[hh0]$ branch where the discrepancies between theory and experiment are most pronounced and it is certainly appropriate to say that earlier work largely fails to predict the correct behavior of this branch.

More recently, the most convincing calculations of anharmonic phonon-frequency shifts in alkali metals have been performed by Vaks and co-workers^{14,15} (Ref. 14 contains also a good survey of earlier work in this field). They obtain a variation of the frequency shifts in lithium and sodium over the entire $\sum_4[hh0]$ branch which is in good qualitative agreement with available ex-

perimental data and also gives the correct order of magnitude. It should be emphasized, however, that in discussing their results Vaks *et al.*—contrary to earlier less successful work—definitely relate the softening of the N'_4 mode to the phase transition from the bcc to the closed-packed phases.

With regard to the above-cited examples of substances which soften, however, do not transform we only remark that the softening and other anomalies observed in Pb, Nb, and TaC (see, e.g., Refs. 16–18) are remote from the phenomena found in alkali metals and, therefore, of little value in the present context (e.g., lead exhibits an fcc structure, there are two other phonon branches which soften and lie still lower than the $\sum_4[hh0]$ branch and, in addition, a Kohn anomaly is involved).

Finally we should like to point to a very recent neutron-scattering study on sodium by Abe, Oshima, Suzuki, Hoshino, and Kakurai¹⁹ whose results are entirely in agreement with our earlier investigation of phonon-frequency shifts as a function of temperature. In particular, the measurements of Abe *et al.* confirm the softening of the $\sum_4[hh0]$ branch for $q \geq 0.25$. The following conclusions summarize the arguments presented so far.

Available experimental evidence including the data provided by Berliner *et al.* does not disprove the softening of the $\sum_4[hh0]$ phonon branch as described by the present authors.²

Contrary to the view expressed by Berliner *et al.* it seems difficult to explain how spin-incoherent elastic scattering may give rise to the peculiar features of the diffuse scattering close to the phase transition as observed by the present authors.

The interpretation of these experimental findings as representing precursor phenomena to the low-temperature phase transition is well justified and also supported by recent independent theoretical work.

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⁴G. Dolling, B. M. Powell, and P. Martel, *Can. J. Phys.* **46**, 1727 (1968).

⁵H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson, *Neutron Inelastic Scattering*, International Atomic Energy Agency, Vienna, 1968, Vol. 1, p. 149 (this is the corrected citation of a misprinted reference in the paper of Berliner *et al.*).

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¹⁵V. G. Vaks, G. D. Samolyuk, and A. V. Trefilov, *Phys. Lett. A* **127**, 37 (1988).

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¹⁷B. M. Powell, A. D. B. Woods, and P. Martel, *Neutron Inelastic Scattering* (International Atomic Energy Agency, Vienna, 1972), p. 43.

¹⁸H. G. Smith, N. Wakabayashi, and M. Mostoller, in *Superconductivity in d- and f-band metals*, edited by D. H. Douglass (Plenum, New York, 1976), p. 223.

¹⁹H. Abe, K. Oshima, T. Suzuki, S. Hoshino, and K. Kakurai, *Phys. Rev. B* **49**, 3739 (1994).