

Effect of pressure on the phase transitions in Li and Na

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The methods of acoustic emission and neutron structural analysis are used to investigate the effect of high pressures on the temperature of the martensitic structural phase transition in Li and Na. It is established that the shape of the phase diagram predicted by Vaks, Kravchuk, and Trefilov on the basis of the local-potential model is in agreement with the experimental data for Na but not for Li.

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In the light alkali metals Li and Na, the bcc lattice becomes unstable at low temperatures and undergoes a martensite-type structural phase transition to the hcp structure.

This circumstance is of significant interest for checking the current microscopic theory of non-transition metals. One of the fundamental problems of the theory is to calculate the stability regions of the crystal structures and the phase-transition points; this problem cannot at this time be regarded as solved even for simple metals. The solution of this problem requires a very precise calculation of the system energy. In the case of Li and Na, for example, the difference between the structure-dependent contributions at zero temperature and pressure amounts to only 10^{-4} – 10^{-5} of the total binding energy.

Moreover, it has been shown in a series of papers² that almost all the known atomic properties of the alkali metals can be described to good accuracy in a unified scheme involving the use of a simple local potential of the Abarenkov-Heine type. The success of this scheme enabled those authors to apply the model with assurance to the description of a number of properties which had not been studied yet, including the structural phase diagrams of Li and Na.¹ Our goal in the present study was to check experimentally the predicted shape of these phase diagrams.

Reliable experimental data on the martensitic transformations in Li and Na had previously been obtained only at normal pressure.³ It had been established that the temperatures at which the transformations begin under cooling of the samples are 70 K in Li and 32–35 K in Na. The temperatures of the inverse transition under heating, 90 K in Li and 45 K in Na, had been determined to lower accuracy. With regard to the transformation under pressure, there was only fragmentary information which was insufficient to determine the phase diagrams.

It should be stressed that the experimental study of these transitions is complicated substantially by features of the martensitic transformation such as the large hysteresis, the incompleteness of the transformation (especially in Na), and the dependence of the results on the previous history of the sample.

For observation during the phase transitions we used the relatively new method

of recording the acoustic emission accompanying the martensite transformation. Neutron diffraction was used to identify the crystal structure of the samples at various stages in the transformation. The experiments were done on an apparatus designed for neutron structural studies under pressure at the Fabel linear electron accelerator.

The investigated samples had a chemical purity of at least 99.9%. To decrease the neutron absorption in the Li we use the separated isotope Li^7 at a content of 99.5%. The high pressure chamber was a cylinder and piston arrangement without a pressure medium. The pressure was measured to within $\sim 5\%$ by the piston-displacement method.

The pressure chamber was cooled in a cryostat by the flow of gaseous helium. By changing the flow rate, we could vary the temperature of the sample from room temperature to 10 K. To detect the acoustic emission we used a TsTS-19 piezoceramic transducer mounted mechanically on the side wall of the pressure chamber.

The phase transition was monitored by observing the acoustic-emission peak which appeared when the sample was cooled at a fixed pressure. The compression of the sample to the necessary pressure was always carried out at a temperature of at least 250 K; this procedure provided a rather effective annealing of defects, which could otherwise affect the temperature of the martensitic transformation.

In the case of Li, the emission peak under cooling was always clearly expressed (see Fig. 1) and permitted us to fix the temperature of the start (M_s) and finish (M_f) of the transformation to an accuracy of several degrees. The peak did not appear during heating of the sample at a constant pressure; this is apparently an indication that the kinetics of the forward and inverse transitions are substantially different.

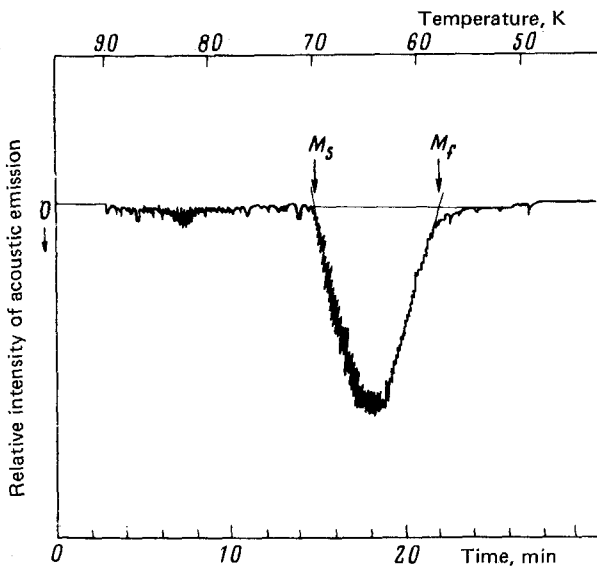


FIG. 1. Acoustic-emission peak during the martensitic transformation in Li under cooling of the sample, $P = 0$.

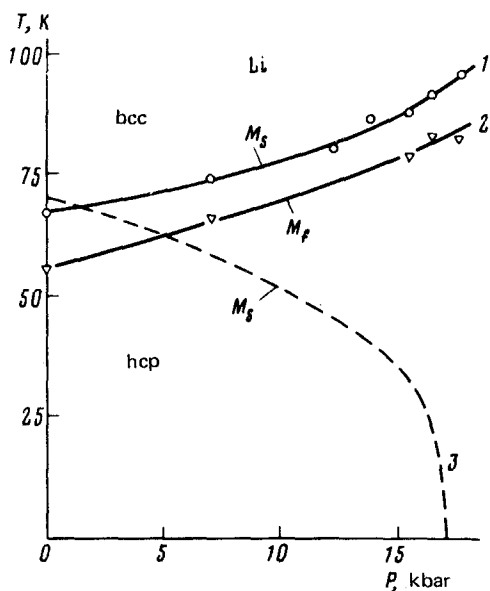


FIG. 2. Phase diagram of Li. 1, 2) Starts M_s and finish M_f of martensitic transformation observed during cooling of the sample at fixed pressure; 3) the calculated value of Vaks *et al.*¹

The Li sample was subjected to three series of neutron-diffraction measurements at normal pressure: before the transition ($T = 90$ K), after the transition ($T = 60$ K), and after an annealing to 250 K ($T = 90$ K). The first and third neutron-diffraction patterns were nearly identical and corresponded to a bcc structure. The second diffraction pattern, in addition to the bcc reflections, contained well-defined peaks belonging to the hcp lattice. Reflections corresponding to the fcc structure were not observed by us. The neutron measurements of the Li were carried out only at normal pressure, since such measurements in the high-pressure chamber are complicated by the considerable attenuation of the neutron beam by the chamber. However, the similarity of the acoustic-emission peaks is evidence that the nature of the phase transition remains unchanged over the entire range of pressures studied.

Figure 2 shows the phase diagram of Li obtained by Vaks *et al.*,¹ together with our experimental results. The diagrams appear to be qualitatively different: The existence region of the low-temperature hcp phase actually widens with increasing pressure, while the calculations predict that it should vanish. This circumstance is also indicated by the ratio of specific volumes of the bcc and hcp phases. Table I gives the lattice parameters of the two phases as determined from the neutron-diffraction patterns, and the corresponding volumes. We see that the hcp phase, which is stable at high pressure, also has the higher density. The x-ray structural measurements of Barrett,³ we might note, imply the opposite result. However, the difference in the volumes in the two cases is within the error limits of the measurements.

The problem of detecting the martensitic transition in Na turned out to be substantially more complicated than in Li, since the transition in this case is less intense

TABLE I. Lattice parameters of Li from neutron-diffraction measurements. $T = 60$ K.

	a , Å	c , Å	V , Å ³ /at	ΔV (bcc-hcp)
hcp	3.096 ± 002	5.038 ± 4	41.82 ± 7	0.14 ± 0.10
bcc	3.475 ± 2	—	41.96 ± 7	

and is shifted toward lower temperatures. The acoustic emission in Na is more sensitive to the previous history of the sample, to the cooling conditions, and to the pressure regulation during cooling. The neutron-diffraction studies of the martensite transformation, which in this case were also carried out at high pressure, were further complicated by the low concentration of the hcp phase. Because of these difficulties, we have not yet obtained as accurate results in Na as we did in Li, and the data shown in Fig. 3 should be regarded as preliminary. Nevertheless, the data clearly show that the shape of the phase diagram in Na is qualitatively different from that of Li and agrees with the calculations of Vaks *et al.*¹

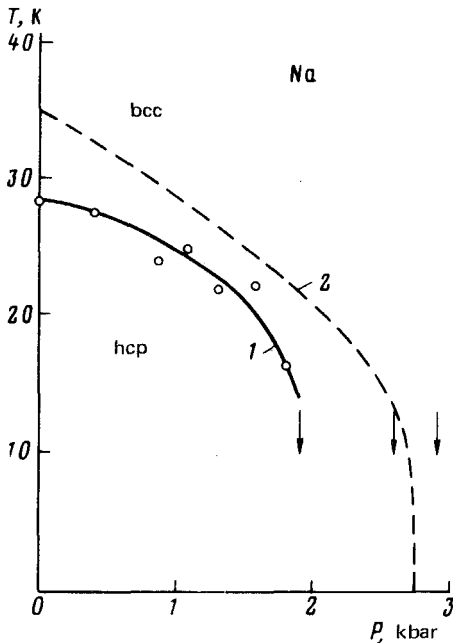


FIG. 3. Phase diagram of Na. 1) Experimental curve $M_s(P)$; 2) calculated¹ curves $M_s(P)$. The arrows indicate pressures at which the acoustic-emission peak was missing at temperatures down to 10 K.

The theoretically predicted pressure effect is thus seen to be correct for Na and incorrect for Li. This result is not surprising, since the other atomic properties of Li are generally described less accurately than those of Na. The reason for these difficulties apparently lies in a appreciable nonlocality of the potential in Li due to the large contribution of the p scattering amplitude, which is not canceled out because of the absence of p electrons.⁶

The electron-ion interaction potential in Na should be extremely simple, and in this case the calculation¹ with a simple model potential does in fact give highly accurate results.

In conclusion, we note that the pressure dependence $M_s(P)$ measured in this experiment is not the true thermodynamic-equilibrium boundary $M_d(P)$ of the two phases, which lies higher: in Li at $P = 0$ we have³ $M_d \simeq 105$ K. It is possible that experiments with variable pressure will permit determination of this boundary. The qualitative behavior of $M_d(P)$, however, should apparently be no different from that of $M_s(P)$.

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