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Ultrasonic propagation above and below the martensitic transition in solid D_2

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The change in the transmitted signal amplitude of longitudinal sound with temperature is studied in D_2 upon thermally cycling a crystal, grown in the hcp phase, between 1.5 K and the melting point, before and after crossing the martensitic hcp-fcc transition. These and other experiments lead to the conclusion that an intermediate close-packed structure is progressively stabilized at the expense of the cubic phase above the transition until the melting point. This is contrary to conclusions from previous experiments and also in striking constrast with the behavior of H_2. The orientation of the stacked planes, where the net sliding occurs during the transition, remains the same as in the original hcp crystal, but within each plane, the structure is undetermined.

I. INTRODUCTION

There has been considerable interest for a number of years in the martensitic hcp-fcc transition in molecular crystals, in particular H_2 and D_2 (Refs.1–7) and ^4He (Refs. 8–10). In the hydrogen crystals upon cooling, the transition from the initial hcp to the cubic phase is driven by the orientational ordering transition of the molecules with rotational angular momentum $J=1$, o-H_2, and p-D_2. This ordering is caused by the intermolecular electric quadrupolar interaction and takes place for concentrations $X(J=1)>0.53$.[11,12] For lower X, the ordering proceeds in a continuous way[13] within the hcp (Refs. 5 and 6) phase upon lowering the temperature. For the hydrogens, the total free energy change between hcp and cubic structures due to the orientational ordering is much larger than from the intrinsic spatial lattice contributions. In ^4He under pressure larger than 1 kbar, a martensitic transition from cubic to hcp is observed upon cooling.[8,9] Mills and Schuch[14] were the first to determine these structures at 3.5 kbar. Here the transition is driven by the difference in the lattice configurational free energies.

The martensitic transition in the hydrogens, reviewed in detail by Silvera,[11] has been investigated by x-ray[1,5] and neutron[7] diffraction, pressure,[2,3] acoustic propagation,[4] and also NMR relaxation and line-shape experiments.[15,16] Recently, acoustic experiments on H_2 were described, and the contrasting behavior of H_2 and D_2 was reviewed.[6] The conclusion was that, starting from an hcp single crystal of H_2 grown at the melting curve, repeated thermal cycling through the transition always recovers an hcp crystal with the same axial alignment, very probably the same crystal as before. This conclusion is reached from the received sound amplitude and from the velocity, both indicating no significant change above the transition before and after the cycling. A small change in the velocity would have signaled a variation in alignment, since the velocity is quite anisotropic both in H_2 and in D_2.[17] The alignment is conserved presumably because the sliding of the nets during the phase transformation is always in a plane having the same orientation. This recovery of the hcp crystal with its original alignment is also observed in ^4He.[9] For D_2, the situation is different in that an original hcp crystal is not recovered above the transition after thermal cycling. Rather, the cubic phase becomes stabilized upon repeated slow thermal cycles through this transition.[1] Furthermore, very recent NMR line-shape experiments (Ref. 18) on single crystals 0.5 K above the transition have led to the conclusion that the orientation of the sliding planes is not changed between the original hcp and the resulting structures. As the temperature increases, x-ray experiments[1] indicate that the cubic phase is progressively replaced by some intermediate close-packed structures. The x-ray apparatus was not suitable for identifying the possible structures, and no corresponding reflections were reported.[1] At about 9 K Schuch *et al.*[1] report that the hexagonal solid begins to reappear and that at 12 K most of the original hexagonal x-ray intensity is recovered. Acoustic measurements[4] indicated that the received sound amplitude of the original D_2 hcp crystal was never reached again upon warming the sample up to the melting curve after it was cycled through the martensitic transition. However, except for a brief qualitative description, neither of the two studies[1,4] gave detailed information on the region above 4 K.

The purpose of the present paper is to describe a new series of acoustic measurements where particular attention has been paid to the temperature region between the martensitic transition and the melting curve. Our plan was also to study the time dependence of the received sound intensity at several temperatures after cycling though the transition, in order to get information on the transformation dynamics, and to compare the behavior of several crystals both of H_2 and D_2.

II. EXPERIMENT

Our experiments used a cell similar to those described in Refs. 4 and 6. The quartz transducers had a diameter of 0.5 cm, and the sound propagated through a cylindrical cavity of 0.3 cm diameter, but with a spacing between the quartz emitter and receiver of 0.6 cm instead of the previous 2 cm and 1.2 cm.[4,6] The reason for choosing a smaller spacer was to improve the probability of growing a crystal transmitting the sound to the receiving transducer without reflection from the cavity wall, and also to increase the sound signal amplitude. Longitudinal sound waves were produced at a frequency of 10 MHz, and the measurement consisted simply of monitoring the amplitude of the first received peak for a constant amplitude of the generated sound wave.

The crystals were grown at a pressure of approximately 110 atm along the melting curve. The calculating pressure drop at constant volume in the solid phase between the melting curve and 1 K, based on data of Ref. 3, was less than 60 atm, and therefore the crystal did not detach from the transducers when the temperature was decreased. (These conditions are in contrast with those of the x-ray work[1] where the crystal was at ~1 atm pressure.) For the growth process, a temperature gradient was established whereby the cell temperature was lowest and the fluid inlet capillary was kept unblocked by means of a heater. The quality of a crystal was assessed from the amplitude and shape of the received signal. Once a satisfactory crystal was obtained, it was annealed up to two hours at a temperature just below the melting curve before being slowly cooled towards the transition. As in previous work,[6] the shape of the received signal was recorded and stored by a microcomputer. Simultaneously, the amplitude of the first received signal was registered by means of a boxcar integrator and plotted on a chart recorder versus temperature or versus time.

Our experimental procedure consisted in first confirming previous experiments on the martensitic transition in H_2 and in extending the acoustic measurements up to the melting curve. The sequence of experiments was as follows. First, the new annealed hcp crystal with $X=0.75$ was slowly cooled to a temperature of ~2 K without crossing the transition, and then slowly heated over a period of 2 h up to the melting curve while the received signal intensity and shape were being continuously monitored. Second, the crystal was again cooled, but this time it was thermally cycled several times over the range from 1.3–2 K through the transition and slowly warmed up to the melting curve. For solid D_2, the same procedure was used, but the thermal cycling was over the range from 1.3–3 K.

III. RESULTS AND DISCUSSION

In the ordered (cubic) phase of H_2, the received amplitude decreased to zero, confirming previous experiments.[4,6] The "control" results on H_2 are shown in Fig. 1. Within a small deviation, the received amplitude in the disordered phase is essentially reversible upon decreasing and increasing the temperature, before and after the martensitic cycling. The original hcp H_2 crystal has been regrown after several thermal cyclings. We also note that there is always a temperature difference $\Delta T = T_{ch}\text{-}T_{hc}$ between the cooling transition $T_{hc}(X)$ and the warming transition $T_{ch}(X)$,[1,2,6] where the subscript *hc* stands for hexagonal-to-cubic and *ch* for the reverse. As in previous experiments,[1,6] ΔT stayed roughly constant during the cycles, while the transition temperatures decreased because of the $(J-1)$-to-$(J=0)$ conversion, with $\delta X/\delta t \approx -1\times 10^{-2}\ \text{h}^{-1}$. A similar experiment with a second H_2 crystal led to the same conclusion.

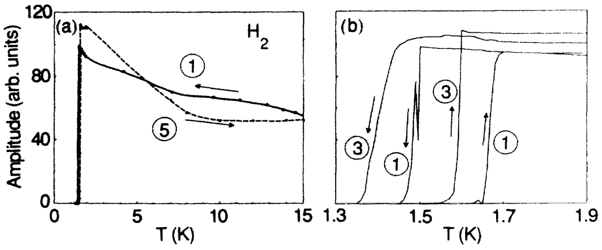

FIG. 1. Received signal height for a H_2 crystal with $0.71 < X < 0.75$ vs temperature upon thermal cycling (a) after passing through the transition several times. Throughout all the figures, the circled number *n* denotes the *n*th thermal cycle. (b) Details of the repeated thermal cycling through the transition where the difference in temperature scales is to be noted. During one cycling between 1.3 and 1.9 K, X decreased from ~0.73 to ~0.72. The average duration of each cycling was ~40 min.

For D_2, the concentration decreased via $(J=1)$-to-$(J=0)$ conversion from $X=0.72$ to 0.68 during the experimentation with four crystals with $\delta X/\delta t \approx -4 \times 10^{-4}\ \text{h}^{-1}$. Here again a control experiment confirmed that the received signal amplitude for the original hcp crystal is reversible over the temperature range between 3 K and the melting curve before any passage through the transition. Cycling through the transition with periods of approximately 1 h, and over the range 1.5 K $< T <$ 3 K, showed, however, striking differences from H_2, is namely:

(1) The amplitude of the received signal did not drop to zero upon transition into the ordered phase.

(2) On successive cycles, the temperature difference ΔT tended at first to increase.

(3) After four cycles in crystal II (six and four cycles in crystals III and IV) the cooling transition T_{hc} was suddenly raised to T_{ch}. This coalescing of T_{hc} and T_{ch} was already reported previously.[3,4] The observations for crystal II are illustrated in Fig. 2(a) for the first series of thermal cyclings. There are qualitatively similar diagrams obtained with crystals III and IV. A clearly detectable change in the received sound amplitude was seen at the transition, although we must assume from the x-ray information[1] that the cubic phase remains largely stabilized just above T_{ch}. An interesting question is therefore whether this observed change—with hardly any hysteresis—is mostly due to the orientational ordering within the cubic phase.

The behavior above T_{ch} showed the same trend with temperature in the three D_2 samples, although to a different extent (Figs. 3–5). As T increased above T_{ch}, the received signal amplitude increased up to approximately 5–8 K. (In crystal II the amplitude previously observed with the original hcp crystal was actually reached at 8 K). This seems to indicate that the proportion of hcp was increasing with T, which is consistent

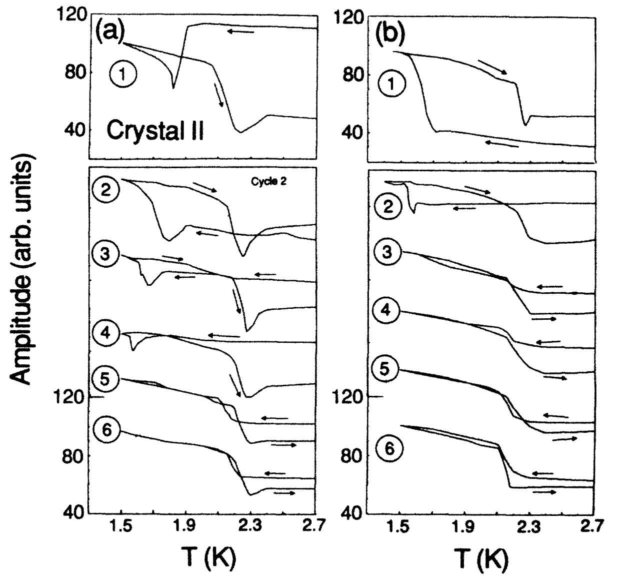

FIG. 2. (a) Received acoustic signal amplitude for D_2 crystal II vs temperature during the first series of cyclings through the martensitic transition. (b) The same during the second series of cyclings. The average duration of each cycling was ~40 min.

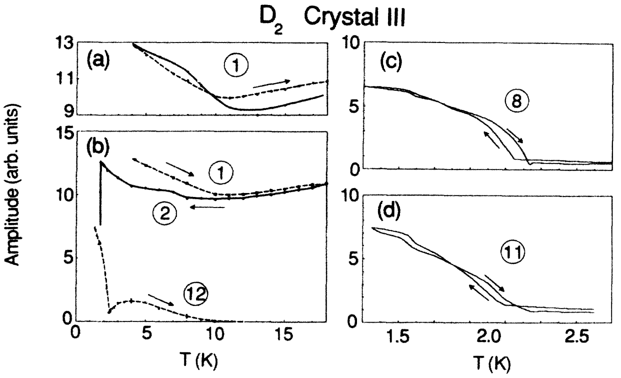

FIG. 4. Received signal height for D_2 crystal III with $0.70 < X < 0.71$ vs temperature upon repeated cycling (a) without passing through the martensitic transition, (b) after passing through the transition several times, and (c) and (d) details of the repeated thermal cycling through the transition. In (a) and (b) cooling and warming is indicated by solid and dashed lines, respectively.

with the observation reported by Schuch *et al.*[1] When observing the signal at constant temperature as a function of time, the amplitude tended to increase until some equilibrium value was reached (Fig. 6). However, above 8 K the amplitude in all cases decreased with increasing T and tended to disappear. Also, at constant T the amplitude decreased with time towards an equilibrium value (Fig. 6). These very unexpected observations then implied that the proportion of hcp single crystal diminished as T increases beyond 8 K, which leads to a larger scattering of sound by lattice imperfections. As time proceeds there appears to be no coherent net sliding activity to restore the original hcp crystal.

The behavior of crystal II on a subsequent cooldown past T_{hc} was very striking. The signal amplitude progressively increased with decreasing T, and suddenly below T_{hc} the amplitude previously observed in the cubic phase was recovered, as shown in Fig. 3(b). A second series of thermal cyclings through the transition was performed as shown in Fig. 2(b), with very similar results to the first series, Fig. 2(a). Hence, the same cubic crystal as before seems to have been obtained.

Finally, the sample was warmed towards the melting point and qualitatively the same behavior as before was observed: Above the transition, the signal at first increased with T, indicating a tendency to regain the original hcp phase. With further temperature increase above 8 K, the amplitude decreased, implying more sound scattering through an intermediate close-packed structure that is progressively stabilized—instead of the hcp. From NMR experiments,[18] we can stipulate that the orientation of the stacked planes in which the sliding occurs is the same as the basal plane in the original hcp crystal. This orientation is the only conserved quantity

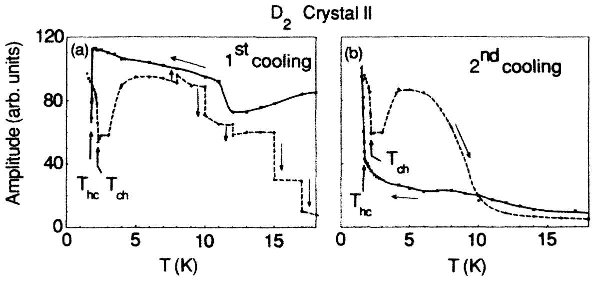

FIG. 3. (a) Received signal height for D_2 crystall II with $0.71 < X < 0.72$ vs temperature upon cooling (solid line) and warming (dashed line) after passing through the transition several times. Here the vertical arrows indicate the temperature where the intensity was monitored as a function of time. (b) The received signal amplitude upon cooling the cycled crystal from 18 K down to 1.5 K and subsequent warming up again, after a second series of thermal cyclings through the transition.

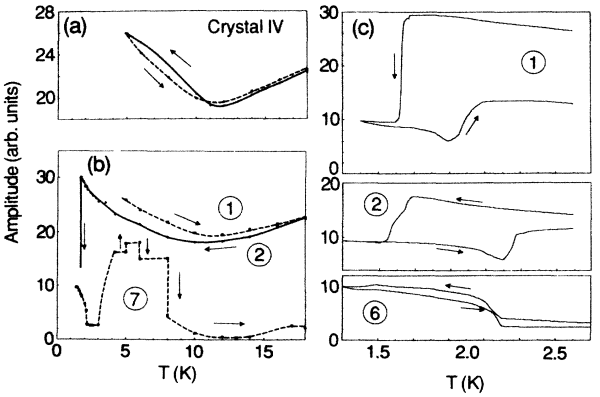

FIG. 5. Same display as in Fig. 4, but for D_2 crystal IV. The vertical arrows indicate the temperatures where the intensity was monitored as a function of time.

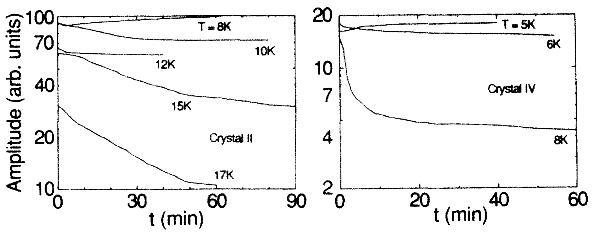

FIG. 6. Time dependence of the recorded signal height for D_2 crystals II and IV at various temperatures.

during the cycling. Within the planes, there might be small ordered domains, but no long-range periodicity, a sort of two-dimensional amorphous system.

In previous papers dealing with NMR (Refs. 19 and 20) and acoustics (Ref. 6) in the cubic phase of H_2, the process of orientational ordering was discussed in relation to the martensitic phase transformation. Since it is known for x-ray work[1] that there always remains a small fraction of hcp disordered phase in the sample, there was the hypothesis of a "skin" of hcp between cubic domains. This skin then acts as a memory to regrow the single crystal of hcp upon warming the sample through the ordering transition. The energy barrier to form the hcp is then presumably small. In D_2, the hcp "skin" between the cubic domains in the ordered phase is apparently unable to initiate the growth back into the bulk hcp, and only an intermediate phase results in the end, from which the cubic phase is regrown upon cooling. The energy barrier to form back the hcp must therefore be much larger than in H_2.

In an earlier paper[6] it was suggested that the difference in the lattice spacing between H_2 and D_2, respectively, 3.78 and 3.60 Å, played an important role in producing a different energy barrier in the net plane sliding process. For H_2, it was argued that this energy barrier ΔE was less than $\Delta E / k_B = 0.5$ K, while it was at least an order of magnitude larger in D_2. By contrast, in ^{4}He the lattice constant is 3.05 Å for 1.1 bar,[8] at which pressure the hcp crystal is restored[9] and there are no oriented molecules to promote or impede the transition. The sliding of the net planes therefore appears to be much easier in ^{4}He at a considerably smaller lattice constant, and must be attributed to the larger zero-point motion.

IV. CONCLUSIONS

In our experiments, performed under conditions of constant density, an original hcp H_2 or D_2 crystal underwent a number of temperature cycling processes through the martensitic hexagonal-cubic transition. Our "control" experiments with H_2, extending previous ones[1,4] to higher temperatures, indicate that the original hcp crystal is recovered above the transition. The D_2 samples showed a very different behavior and our conclusions are as follows.

(1) The received sound amplitude in the cubic phase of D_2 is usually much larger than in H_2 at comparable concentration of $X(J=1)$. This implies that in D_2, the cubic structure has fewer dislocations (or much larger domains) than in H_2.

(2) In none of the three D_2 samples, all cycled through the transition, was the original hcp crystal regrown between T_{ch} and the melting curve. Some sliding of the nets must have occurred, as inferred from the strong temperature variation of the acoustic signal amplitude in the samples. It is near 8 K that the reconstruction of hcp came closest to being realized, but this structure was lost again as the temperature increased further. The intermediate close-packed structure that is apparently stabilized must have many dislocations because of the considerable scattering of the sound it produces. Even the thermal activation near the melting curve was unable over a period of several hours to bring about a coherent sliding of nets necessary to reproduce the original hcp crystal integrally. This result appears to be at variance with earlier findings[1] at atmospheric pressure, which implied that the hcp phase eventually is recovered at high enough temperatures.

(3) However, the intermediate close-packed structure, stabilized at high temperatures, has no difficulty in converting back into the cubic phase below the temperature of the martensitic transition. The received signal intensity is the same as before, implying that the same crystal has been produced again. Together with the information from x-ray NMR, this result implies that the orientation of the stacked planes in which net sliding occurs, remains always the same once the original hcp crystal is formed. This permits the sliding back from the intermediate structure into the cubic phase which is more readily reproduced than the hcp. A possible scenario would be that small cubic domains persist in the intermediate structure and they act as seeds for growth to large cubic domains as the temperature decreases.

It would be interesting to find out what is the origin of the difference between the behavior of H_2 and D_2 and which is the mechanism that prevents the D_2 sample from being grown back into the original hcp crystal in the orientationally disordered phase. A clue to this might be sought in experiments on plastic deformation, for which only data for H_2 (Refs. 21) are available. Another clue might be the equilibrium concentration of vacancies that is larger in H_2 than in D_2.[22] The question whether the density difference between H_2 and D_2 plays a role will be addressed by acoustic measurements in H_2 under pressure, where the same density as in D_2 will be reached.

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