PHYSICAL REVIEW B VOLUME 55, NUMBER 18 1 MAY 1997-II

Influence of small uniaxial strains on the martensitic phase transition in alkali-metal systems

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(Received 6 February 1997)

A neutron scattering investigation of the influence of a uniaxial elastic deformation on the martensitic phase transformation in the alkali-metal systems Li and $\mathrm{Li_{10\,at.\%}Mg}$ is described. The experimental results show that a small but symmetry-breaking elastic deformation of the bcc matrix drastically promotes the phase transformation. The deformation further induces a significant reduction of the otherwise large transformation hysteresis in a virgin crystal and leads to a memory effect; i.e., the hysteresis remains small when the applied elastic strain is released. Moreover, the applied deformation of about 0.1% of the lattice parameter induces a softening of the transverse acoustic $\mathrm{TA_1}[110]$ phonon branch of several percent. The results are compatible with a description of martensitic nucleation in alkali metals as being triggered by strain fluctuations. [S0163-1829(97)05218-1]

I. INTRODUCTION

The bcc instability of alkali metals was extensively studied in recent years and is characterized by the following features. The alkali metals show complicated low-temperature phase diagrams where different close-packed structures coexist within a narrow temperature range.[1–4] In Na a faulted hcp (AB) phase, which may also be described as a long-period polytype phase,[5] together with a $9R$ ($ABCBCACAB$) structure is found. In Li $9R$, fcc (ABC) and a polytype structure are observed where the stacking sequence of close packed planes is disordered. In the alloy $\mathrm{Li_{10\,at.\%}Mg}$ a $9R$ structure is formed.[6]

All alkali metals are characterized by a low-energy transverse acoustic phonon branch $\mathrm{TA_1}[110]$ polarized along $[1\bar{1}0]$ and corresponding to the elastic constant $c'=(c_{11}-c_{12})/2$. This phonon branch shows a mild softening when the temperature is decreased and the system approaches the phase transition.[7–9]

The question arises whether the different and complicated structural features observed are determined by coherency stresses between the bcc matrix and the low-temperature phase as recently proposed for the $7R$ structure in NiAl which was described as an adaptive martensite phase.[10]

In order to get insight into this question we started a program on the influence of elastic uniaxial deformation on the phase transition behavior. We applied an uniaxial compression along the [001] bcc direction, inducing a lattice expansion along [110] and $[1\bar{1}0]$ directions. Nuclei of the low temperature phase likewise induce a similar symmetry-breaking deformation, i.e., a compression along [001] and an expansion along [110] directions.[16,13] The applied elastic uniaxial deformation therefore lowers the coherency stresses and should facilitate the formation of the low-temperature phase.

In the literature the effect of a uniaxial [001] deformation on the phase transformation has been investigated for a NiAl (Ref. 11) and a $\mathrm{Cu_3Al}$ (Ref. 12) system. First results obtained on Li metal show that the elastic deformation promotes the phase transition despite the fact that the elastic strain which could be applied was only about 0.1% of the lattice parameter of the bcc unit cell.[13] On the other hand, the $9R$ structure which was still observed is more stable than expected. We have continued the investigations on Li metal and a $\mathrm{Li_{10\,at.\%}Mg}$ alloy and in this paper we present results showing a strong influence of an elastic uniaxial deformation of the bcc matrix on the phase transition behavior. The $\mathrm{Li_{10\,at.\%}Mg}$ alloy was chosen because of its higher yield strength, permitting an elastic deformation of about 0.3% of the lattice parameter at low temperatures. The results may indicate that the martensitic phase transition in alkali metals is driven by strain fluctuations.

II. EXPERIMENT

The neutron scattering measurements were performed at the triple-axis spectrometers 4F and VALSE, both located at cold neutron source positions of the Laboratoire Leon Brillouin in Saclay (France). An incident neutron wavelength of 2.36 Å was used and a pyrolytic graphite filter was put into the beam in order to remove higher-order contaminations. The monochromator and analyzer were pyrolytic graphite crystals. The collimations were 30 min. As samples single crystals of Li and $\mathrm{Li_{10\,at.\%}Mg}$ were used. An apparatus was used which allows one to apply pressure along the vertical axis of the sample mounted onto a closed-cycle cryostat.

III. PHONON MEASUREMENTS

A Li single crystal was cooled down to 100 K and uniaxial pressure was applied. The deformation induced no plastic flow of the crystal as borne out by the unchanged mosaic spread. Frequencies of the transverse acoustic

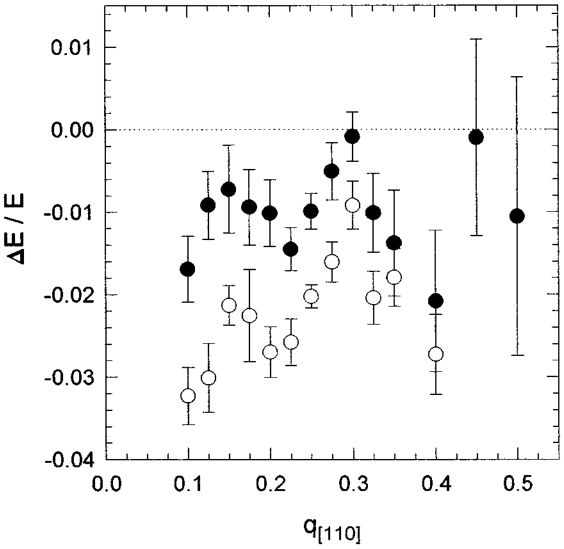

FIG. 1. Strain-induced relative phonon frequency shifts for the transverse acoustic $TA_1[110]$ phonon branch in Li metal. The data points marked by the solid symbols correspond to a lattice expansion along [110] of 0.07%, open symbols to 0.13%.

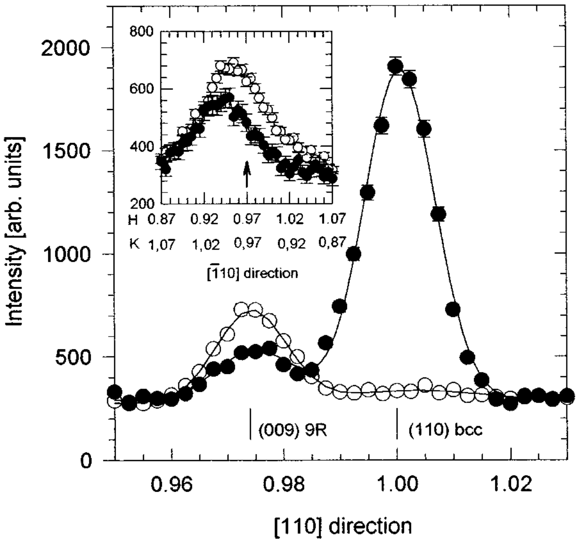

FIG. 2. Radial scans performed along [110] bcc direction in $Li_{10\,\mathrm{at.\%}}Mg$ under applied strain: (●) 120 K and (○) 50 K. The inset shows corresponding tangential scans through the (009) 9*R* reflection.

$TA_1[110]$ phonon branch were measured under elastic compression and for comparison without pressure. The relative phonon frequency shifts were determined following an evaluation procedure described in Ref. 14. The results in Fig. 1 show a softening of a few percent of the whole phonon branch but most pronounced for the low-*q* phonons coming about under the action of elastic strains corresponding to 0.07% and 0.13% of the bcc lattice parameter, respectively. The measured phonon frequency shifts indicate a significant effect of a small elastic deformation on the phonon behavior.

IV. PHASE TRANSFORMATION UNDER STRAIN

Second, we investigated the action of a uniaxial deformation on the phase transition of a LiMg system. In a virgin LiMg crystal the phase transition occurs near 90 K on cooling without pressure whereas the back transformation, exhibiting a large hysteresis, starts above 150 K on heating.[13]

The LiMg single crystal was cooled to 135 K and a uniaxial elastic pressure of 13 MPa, inducing a lattice expansion of 0.18% along [110], was applied. The intensity of the (110) bcc reflection was monitored by rocking scans. Likewise, scans were made near (0.94,1,0) and (1,0.94,0) reciprocal lattice positions where the (009) 9*R* reflections of the low-temperature phase were expected to occur.[6]

After application of pressure at 135 K the scans showed the formation of a small amount of the low-temperature phase. Still under pressure the system was then cooled to 125 K and an increase of the (009) 9*R* intensities was observed. At 125 K a further increase of the elastic deformation (up to 0.3% of the lattice parameter) induced an increase of the (009) 9*R* intensities. The pressurized crystal was then cooled down in steps to 50 K. At 50 K neither an intensity of the initial (110) bcc reflection nor a (110) bcc Debye-Scherrer line could be detected (Fig. 2). Apparently, the bcc matrix had completely transformed. A search for (104) 9*R* reflections revealed corresponding intensities tilted a few degrees out of the original (001) bcc scattering plane. The search confirmed that in this completely transformed material a 9*R* structure is formed.

An investigation of the (009) 9*R* intensities revealed a single broad peak. The (009) 9*R* reflection is located near the [110] direction of the original bcc matrix. The inset of Fig. 2 shows that in the completely transformed system the intensity maximum is tilted by about 0.7° out of the [110] bcc direction. An investigation of the second (009) 9*R* variant near the $[1\bar{1}0]$ direction revealed a similar small misalignment with the $[1\bar{1}0]$ direction. Both 9*R* variants describe within the scattering plane an angle of 91.5°.

These features are at variance with results obtained without pressure where a bcc matrix is still present and where the [009] reflection is found to split up into four variants, each of which is tilted a few degrees out of the [110] bcc direction.[8,1,6] In the case of unstrained LiMg the four 9*R* varaints observed near one [110] bcc reflection are tilted 1.75° out of the [110] direction.[6]

No changes could be observed after removing the pressure. The LiMg system was then heated to higher temperatures where at 140 K the back transformation to the bcc phase occurred. The application of uniaxial pressure to the virgin crystal therefore induced a drastic reduction (65%) of the generally large hysteresis of the phase transformation (Fig. 3).

V. INFLUENCE OF ELASTIC STRAIN ON THE TRANSFORMATION HYSTERESIS

Furthermore, we investigated more extensively the influence of the uniaxial elastic strain on the hysteresis behavior. The crystal was cooled down again and the amount of the bcc matrix was monitored by a measurement of the (110) bcc reflection. In a subsequent cycle the uniaxial pressure was applied on cooling and again a drastic increase of the transition temperature was observed (Fig. 3). The pressure was

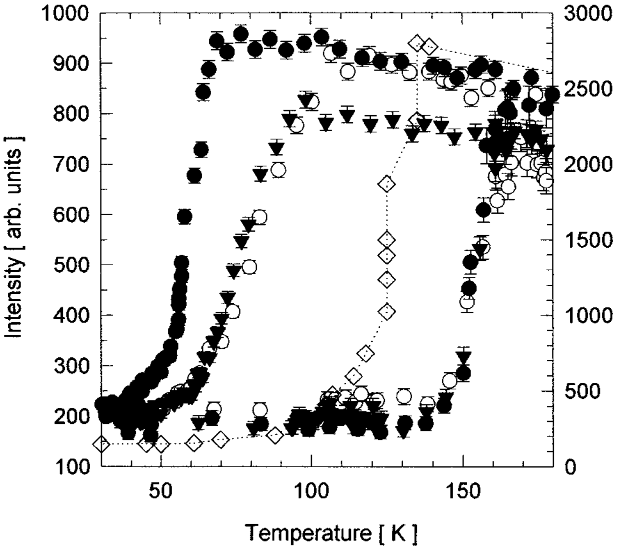

FIG. 3. Transformation cycles as measured by the peak intensity of the (110) bcc reflection in the first $Li_{10\,at.\%}Mg$ crystal: The data points should be followed in a counterclockwise sense. (◇) first cooling with elastic uniaxial strain applied (the scale for this cycle at the right side of the figure), (●) second cooling and heating without applied strain, (○) third temperature cycle with applied strain, and (▼) fourth temperature cycle without applied strain.

removed and a further cycling without pressure yielded a transformation hysteresis only slightly larger than observed during the cycle performed before under pressure. Another cycling through the phase transition induced no further changes in the hysteresis behavior.

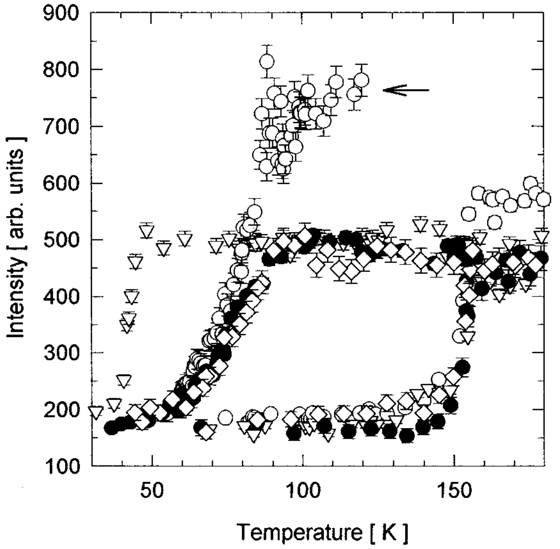

FIG. 4. Transformation cycles as measured by the peak intensity of the (110) bcc reflection in the second $Li_{10\,at.\%}Mg$ crystal: The data points should be followed in a counterclockwise sense. The horizontal arrow indicates the start point of the measurements. (○) first temperature cycle without elastic strain applied, (▽) fourth temperature cycle without elastic strain applied, (●) fifth temperature cycle with applied elastic strain, and (◇) sixth cooling and heating without applied strain.

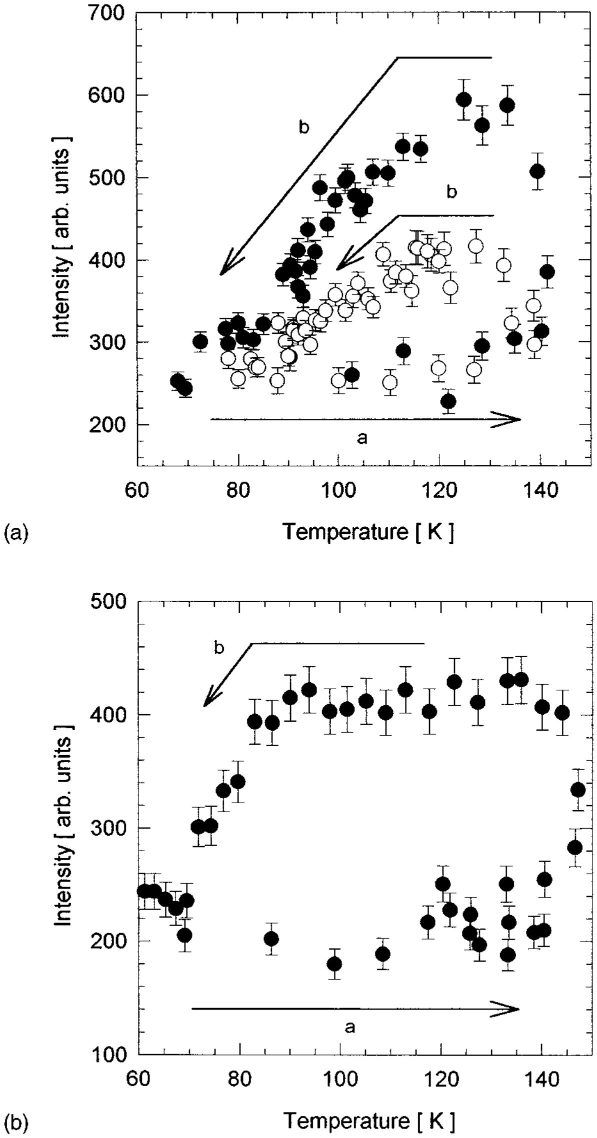

FIG. 5. (a) Transformation cycles as measured by the peak intensity of the (110) bcc reflection without applied strain in crystal 2 after the sixth temperature cycle shown in Fig. 4. The cycles were started at low temperatures where the system was transformed. On heating (arrow *a*) the recovery of the bcc phase near 140 K was arrested by cooling the system down again (arrow *b*). The two symbols describe data of temperature cycles corresponding to two different stages of recovery of the bcc phase obtained near 140 K. (b) For comparison transformation cycle measured in crystal 2 after the first cooling cycle. The cycle starts at low temperatures where the system was transformed. On heating (arrow *a*) the back transformation to bcc was arrested near 140 K by cooling the system down again (arrow *b*). No elastic strain was applied during the cycles.

We pursued the investigations with a new LiMg crystal which was cycled through the phase transition several times without application of pressure. The results confirmed that the hysteresis is smallest in the virgin system and then continuously increases with the number of transformation cycles. After four cycles the crystal transformed near 40 K. Then, during the following cycle, uniaxial pressure was applied on cooling and again a drastic increase of the transition temperature connected with a narrowing of the hysteresis was observed (Fig. 4). After a subsequent pressure release the hysteresis essentially remained reduced and showed no further evolution even after several cycles without pressure.

In this stage where an even narrower hysteresis than in a virgin crystal is observed the system exhibits a quicker response to any temperature change. This is borne out by the transformation curves of Fig. 5(a). Figure 5(a) shows the intensity of the (110) bcc reflection during temperature cycles started at low temperatures where the crystal was transformed and then heated up to near 140 K where the back transformation to bcc started. At 140 K the back transformation was arrested—i.e., at a given intensity level of the appearing (110) bcc reflection the system was cooled down again. Figure 5(a) depicts the measured behavior for two intensity levels of the (110) bcc reflection of the recovered bcc structure, respectively. Near 140 K for both cycles remnants of the low-temperature phase were still present. The curves of Fig. 5(a) show that on cooling in both cyles the phase transition starts immediately after the temperature decrease, indicating that in this stage the remnants of the low-temperature phase act as preferential nucleation sites for the phase transformation. By way of contrast we include the transformation behavior obtained in a normal crystal where no pressure was applied during all cycles of its history [Fig. 5(b)] and where likewise on heating the bcc phase was only partially recovered near 140 K. During the following cooling procedure the transformation to the low-temperature phase started only at significant lower temperatures than shown in Fig. 5(a).

VI. DISCUSSION

The present experiment shows that the application of a uniaxial elastic deformation promotes the phase transformation, considerably reduces the transformation hysteresis, and even induces a memory effect with respect to the hysteresis when the pressure is released.

In the literature many theories of martensitic phase transitions are presently discussed.[15–17,19] Some of these theories exclude nucleation mechanisms based on thermal fluctuations.[18]

The present results suggest that in alkali metals the nucleation mechanism is triggered by thermally activated strain fluctuations which are favored by the low-energy $\mathrm{TA}_1[110]$ transverse acoustic phonon branch. The low-energy phonon branch shows a further softening when the uniaxial elastic deformation is applied which promotes the phase transition. Moreover, the recent observation of incubation times at constant temperature[9,20,13] corroborates the thermal activation of the nucleation process. Once a nucleus of the low-temperature phase is formed it induces a similar symmetry-breaking deformation of the bcc matrix as the one macroscopically applied in this series of experiments. Elastic deformation promotes the phase transformation in all cases and therefore it is very likely that the similar strain field connected with the nucleus of the new phase likewise promotes the phase transformation, thus inducing a self-amplification of the transformation product due to its own strain field. This means that the transformation—once started—does not stop in an embryonic state but runs through the bcc matrix until it is arrested by the elastic energy of the two-phase system.

It further follows that the strain fluctuations favoring the martensitic nucleation should be rather specific (i.e., of $\mathrm{TA}_1[110]$ shear type) in order to promote the transformation. If random strains are present as in a deteriorated plastically deformed crystal[21] after one or several transformation cycles, then it seems that the nucleation is inhibited and consequently starts at lower temperatures, thereby increasing the hysteresis as experimentally observed. Moreover, it was an open question why particles of the low-temperature phase persisting on heating do not act as centers of easy nucleation when the system is cooled down again. It may be conjectured that these particles, persisting at temperatures where alkali metals are easily plastically deformed and where the crystal is deteriorated, are inactivated as nucleation centers since plastic deformation of the bcc matrix around the particles reduces the specific elastic strain field needed for martensitic nucleation.

The memory effect in the hysteresis behavior and its relation to the quicker response of the system under a temperature change are novel and interesting features which should be further investigated. The memory effect observed after application of pressure may be related to an alignment of strain fields connected to an alignment of particles of the low-temperature phase under the action of the applied uniaxial pressure. The alignment of strain fields induces an easier nucleation as shown by the narrower hysteresis.

In summary, we have shown that a small uniaxial elastic compression along a [001] bcc direction induces a significant softening of the $\mathrm{TA}_1[110]$ phonon branch, promotes the phase transformation, and induces a memory effect when the pressure is released. The results suggest that the martensitic nucleation is driven by specific strain fluctuations.

ACKNOWLEDGMENT

Our work was partly supported by the Fonds zur Förderung der wissenschaftlichen Forschung in Austria.

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