Coherent Modulated Structure during the Martensitic hcp-fcc Phase Transition in Co and in a CoNi Alloy

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Diffuse neutron-scattering experiments on the martensitic fcc-hcp phase transition in single crystals of pure cobalt and Co–32% Ni reveal the presence of satellites around (111) fcc reflections within a temperature range where the fcc and hcp phases coexist. The satellites indicate a modulation of the (111) fcc lattice planes with a wavelength $\lambda = 6d_{111}$. This result can be explained by the occurrence of an intermediate structure where platelike nuclei of the hcp phase are coherently inserted into the fcc matrix.

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Martensitic transformations have been the subject of continuously growing interest over many years.[1] Independent of the classical theories based essentially on dislocations,[2] more recent approaches to martensitic transitions include Fermi-surface mechanisms (see, e.g., Bruinsma and Zangwill[3]) and incomplete softening of phonons (e.g., Mori, Yamada, and Shirane[4] and Blaschko and Krexner[5]). In particular, premartensitic effects have been investigated extensively during the last years, such as the "tweed" formation found in NiAl alloys[6,7] and the satellite patterns detected in the shape-memory alloy TiNi(Fe),[8] both of which point to the presence of atomic correlations over considerable distances. In the last case different explanations have been put forward, such as the condensation of phonon modes,[8] lattice discommensurations,[9] and a modulated lattice relaxation model,[10] none of which, however, seems presently beyond doubt.[11]

In the present study results of a neutron-scattering investigation of the martensitic transformations in both pure Co and Co–32% Ni are reported. Pure Co transforms from hcp to fcc near 690 K on heating and Co–32% Ni shows the reverse transformation (fcc → hcp) at about 120 K on cooling. We have observed an intermediate modulated structure within the hcp-fcc two-phase region which exhibits some similarity to the above cited findings in NiAl and TiNi(Fe), though it should be interpreted in a different context.

Both the hcp and the fcc phases of cobalt represent close-packed structures, yet they differ with respect to their stacking sequence. The fcc lattice is made up of (111) planes whose stacking is *ABCABC*.... The hcp (00.2) planes are equivalent to (111) fcc planes but their stacking is *ABABAB*.... Stacking faults causing planar disorder on (00.2) hcp planes are inherently present in hcp cobalt[12] and were often suggested to trigger the transition in some way. However, diffuse neutron-scattering experiments[13] and recent transmission electron-microscopy investigations[14] do not confirm this idea. Various other transformation mechanisms have been proposed which are essentially based on dislocation reactions.[15–17] In several martensitic transformations lattice softening occurs as a precursor phenomenon to the phase transition. Yet a neutron-scattering investigation of the lattice dynamics of fcc Co–8% Fe did not show any decrease of phonon frequencies at low temperatures.[18]

The present investigation was done on the triple-axis spectrometer VALSE located at a cold-neutron guide position at the Orphée reactor at Saclay with an incident neutron wavelength of $\lambda = 0.236$ nm. In order to eliminate higher-order contaminations a pyrolytic graphite filter was used. The first part of the experiment was performed on a Co–32% Ni single crystal with an initial mosaic width of approximately 30 min. Upon cooling, first indications of the onset of the transformation were observed near 170 K when the mosaic width of the sample and also the radial widths of the (111) fcc Bragg reflections were found to increase slightly. A careful investigation of diffuse scattering carried out in a wide region of reciprocal space at 130 K (cf. Fig. 1) revealed satellites at the positions $(111) \pm \frac{1}{6}[111]$ and $(111) \pm \frac{1}{6}[\bar{1}11]$. Compared with the fcc Bragg peaks their intensity is about 10^{-3} and their width is up to 100% larger. Cooling to 100 K made the intensity of both satellites and hcp reflections increase by about 20%. No further change was observed below 100 K. Upon heating, the characteristic features of the scattering pattern were still observable even when the crystal again reached room temperature. Only a subsequent thermal treatment of 2 h at 770 K finally removed the satellites and the hcp reflections. The satellites reappeared when the annealed crystal was cooled down a second time below 150 K. Furthermore, simultaneously with the appearance of the hcp reflections, diffuse streaks along the $[10.\zeta]$ hcp direction were observed showing the presence of stacking faults in the hcp structure even during the early stages of hcp formation.

The second part of the investigation was carried out

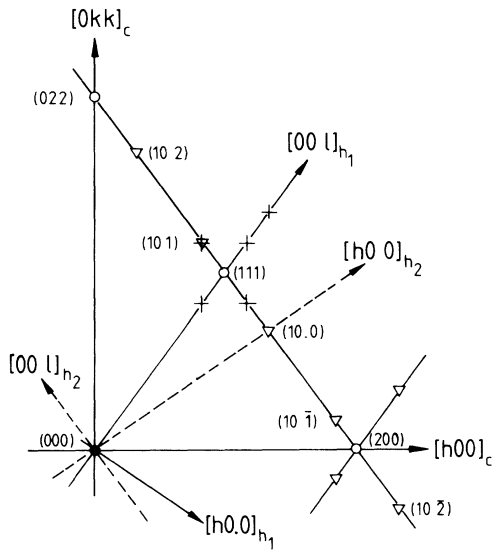

FIG. 1. Elastic-scattering pattern observed in Co–32% Ni at 130 K. Axes are indicated for the two hcp variants. Circles: Fundamental fcc reflections labeled with (*hkl*) notation. Triangles: Fundamental hcp reflections labeled with (*hk.l*) notation. Crosses: Satellites.

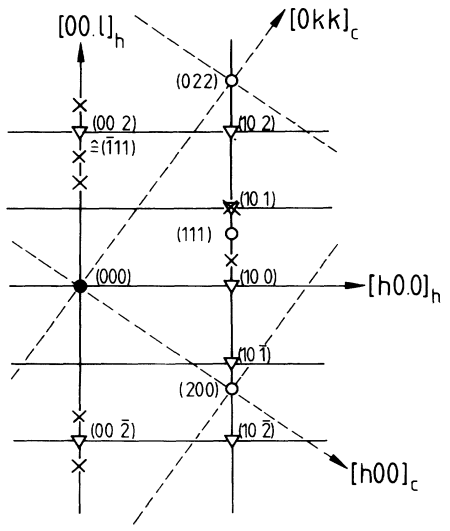

FIG. 2. Elastic-scattering pattern observed in Co at 700 K on heating (hcp→ fcc transition) and at 685 K on cooling (fcc→ hcp transition). Symbols as in Fig. 1.

with a single crystal of pure cobalt. The sample was mounted in a furnace; the initial mosaic width was about 30 min. Because of grown-in stacking faults a diffuse streak along $[10.\zeta]$ was observed whose intensity did not change between ambient temperature and 670 K which is in accordance with earlier work.[13,14] At 700 K fcc reflections developed showing that a large amount of the hcp crystal had transformed to one single fcc variant (two variants are possible). In addition, satellites appeared along $[00.\zeta]$ and $[10.\zeta]$ {corresponding to the $[\bar{1}11]$ and $[(2-\zeta),\zeta,\zeta]$ fcc directions} at a distance of $q \sim \frac{1}{6}\langle 111\rangle$ from the (111) fcc reflections (see Fig. 2). The intensity of the satellites was about 10^{-3} to 10^{-2} of the intensity of the hcp reflections. After heating to 720 K both the hcp reflections and the satellites had disappeared and nearly the entire crystal had transformed to one single fcc variant. Some intensity, however, was also found at positions where the other variant is expected to occur. No diffuse streaks could be detected within the fcc structure. Upon cooling the hcp reflections reappeared at 680 K and also simultaneously the streaks caused by the stacking faults were again observed. The fcc reflections decreased and satellites appeared again at the same positions as before, only their intensities were somewhat different. At 650 K the hcp reflections regained their original intensity and the satellites disappeared. The fcc reflections decreased drastically but could still be detected. Finally, the measured intensities changed only a little when the sample was gradually cooled down from 650 K to room temperature. Even at room temperature very weak reflections of the high-temperature fcc structure were still present ($\sim 10^{-4}$ of the original intensity).

In addition to the first-order satellites, second-order satellites were also found at some of the fcc positions $(111) \pm \frac{2}{6}\langle 111\rangle$. Their relative intensity is about 1 order of magnitude lower (cf. Fig. 3) and depends strongly on the progress of the transformation. Gaussian fits to the satellites of both first and second order always yielded positions which are compatible with a modulation wave vector $\frac{1}{6}[111]$ within experimental error and none of the satellites was found outside the range $\frac{1}{6}$ (or a multiple of it) ± 0.02.

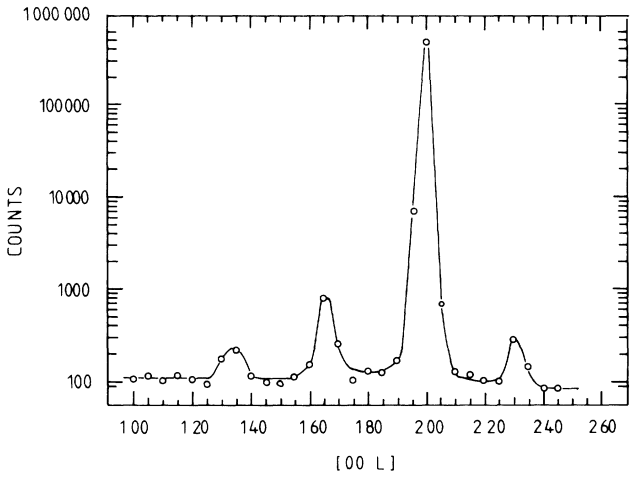

FIG. 3. Elastic radial scan along [00.1] as measured in Co at 700 K. The scattering intensity is given on a logarithmic scale. On either side of the (00.2) Bragg peak [identical with the fcc (111) position] satellites of first order are present centered at $(00.2) \pm \frac{1}{3}[00.1]$. A satellite of second order is found at $(00.2) - \frac{2}{3}[00.1]$.

An investigation of the first-order satellites in Co-32% Ni as a function of the energy of the incident neutron beam up to 30.5 meV performed on a thermal spectrometer invariably gave the same positions in reciprocal space. Therefore, any spurious effects depending on the neutron wavelength, such as multiple scattering, can be excluded. A search around the (222) Bragg peak of Co-32% Ni revealed satellitelike intensity patterns at the same reduced q vectors as in the (111) Brillouin zone. However, because of the higher energies required to scan the (222) zone, these measurements were somewhat impeded by the reduced effectiveness of the graphite filter and the higher background present on a thermal spectrometer.

In order to elaborate the structural features responsible for the presence of the satellites in the two-phase region the following considerations should be taken into account.

(1) Periodic variations of the crystal lattice which affect the stacking sequence but do not lead to a corresponding periodic change of the interplanar distances can entail satellite intensities only along hcp directions $[h0.\zeta]$ with $h \neq 0$. The observation of satellites along the $[00.\zeta]$ direction, therefore, implies that stacking variants such as the well-known $6H$ structure do not furnish the correct interpretation.

(2) The reduced wave vector $q = \frac{1}{6}\langle 111\rangle$ establishing the satellite positions relative to the fcc (111) reflections clearly indicates a modulation of (111) fcc planes with a wavelength $\lambda = 6d_{111}$. The question arises whether a periodic arrangement of stacking faults can be constructed whose strain fields lead to the necessary interplanar distance variation. The origin of a possible strain modulation is easily seen if the stacking sequence is described in terms of the H(hexagonal)-K(cubic) notation, e.g., $ABCBCB = HKHHHK$, while the interplanar distances for H and K planes are assumed to vary. (In the case of Co the distances between close-packed planes belonging to the hcp and the fcc phases differ by about 0.4% at the transition temperature). All stacking sequences which can be constructed in agreement with the above periodicity condition were simulated numerically with a computer program designed essentially along the same lines as the one described by Berliner and Werner.[19] These calculations allow for the difference in the lattice parameters for H and K planes and led to the result that no periodic close-packed stacking sequence gives a scattering pattern in accordance with the experimental data.

(3) Since the satellites are found about the (111) fcc reflections they must be due to a periodic modulation of the fcc volume fraction. On the other hand, the hcp nuclei play an essential role in the formation of the distortion since the satellite intensity varies concomitantly with the intensity of the hcp reflections, at least within a certain temperature range.

Therefore, we propose that the observed satellite pattern is due to a strain-field modulation originating from coherency stresses between the fcc structure and the minority hcp phase. As is well known, the structural features occurring in a solid-state two-phase region are governed by the interplay of surface free-energy terms and distortion energy. According to Khachaturyan[20] long-range modulated structures are favored in cases where the distortion energy is high in comparison with the surface terms. In Co coherency stresses are inherently present because of the mentioned lattice misfit along the c direction. On the other hand, the surface energy between different close-packed structures matching coherently (fcc and hcp) is generally low, which is also borne out for Co by experiments.

In order to decrease the distortion energy caused by the difference in lattice parameters along the hexagonal axis the minority phase will form lamellae perpendicular to this direction. Their thickness is determined by coherency stresses which are particularly small for hcp inclusions consisting of six layers[21] as explained in Fig. 4. The hcp platelets can easily grow or shrink in directions parallel to the basal plane depending on the progress and direction of the fcc-hcp transition. On the other hand, structural changes along the c direction are difficult since they rapidly engender an increase of distortion energy. This last structural feature is also sup-

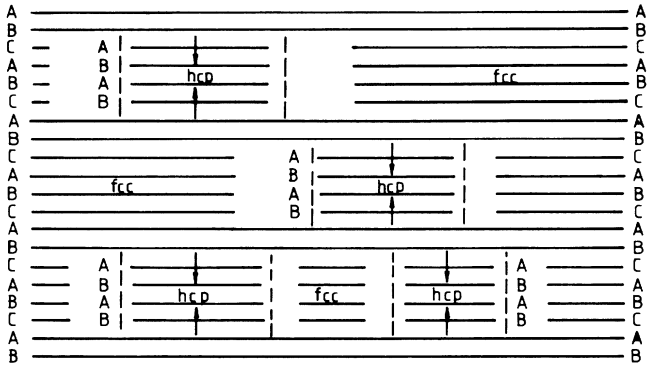

FIG. 4. Schematic representation of hcp nuclei coherently inserted in the fcc matrix. At the left and right sides the stacking sequence of the fcc lattice ($ABCABC\ldots$) is indicated. The stacking of the hcp structure ($ABAB\ldots$) as marked beside the hcp inclusions develops by way of $\frac{1}{6}\langle 112\rangle$ shears on every other fcc plane. After three shears (i.e., six planes) the stacking sequences of the hcp and the fcc structure coincide again which is symbolized by continuous lines. The partial dislocations corresponding to the shears give a resulting Burgers vector $\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3=\mathbf{0}$ thus avoiding long-range stresses. The arrows within the nuclei point to the fact that the interplanar distance of the hcp phase is slightly smaller than for the fcc structure thus causing strains which we believe to be at the origin of the modulation of the surrounding matrix. The nuclei are not drawn to scale. They will generally extend relatively far parallel to the close-packed planes thereby creating lamellae characterized by a large surface-to-volume ratio.

ported by the experimental data. The satellite intensities are roughly proportional to the hcp volume fraction but the widths are nearly unchanged indicating that the extension of the modulated regions along the hcp c direction (or $\langle 111 \rangle$ fcc) does not vary strongly. From the widths of the satellites their size can be estimated to be about 10–30 nm.

The cited effects observed in NiAl and in TiNi(Fe) (Refs. 6–10) resemble the results of the present investigation in that small inclusions being structurally different from the matrix are supposed to be at the origin of the long-range modulation causing the respective scattering pattern. Both in NiAl (Ref. 7) and TiNi(Fe) [22] the phase transition gives rise to marked changes in the phonon dispersion curves. We have investigated the behavior of longitudinal and transverse phonons along (111) in Co–32% Ni as a function of temperature; however, no significant effects could be observed.

The most conspicuous feature of the transition region is the long-range coherence of the modulated lattice resulting in satellites whose widths are rather small. We would like to stress that characteristic aspects of the atomic rearrangements leading to the phase change can be inferred from this observation. Finally, we think that the shape-memory effect occurring during this transformation is also in agreement with the present findings. The formation of a long-range coherent structure during the transition favors the final growth of a single variant of the new phase as indeed observed.

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