Martensitic phase transformation and lattice dynamics of fcc cobalt

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The phonon dispersion of the high-temperature fcc phase of pure cobalt has been measured by inelastic neutron scattering at 833 K. Transverse phonon branches were measured above and below the Martensitic hcp-fcc transformation in order to learn about an influence of lattice dynamics, if any. No new anomalies could be observed, except those confirming an anomalous decrease of the c_{44} (hcp) shear constant when approaching the transformation from below and those confirming a transverse $T[00\xi]_{\text{hcp}}$ and $T[\xi\xi\xi]_{\text{fcc}}$ branch of relative low energy. The small shear constant and results from an analysis of elastic diffuse and Bragg data can be understood in the framework of a dislocation-driven transformation mechanism proposed by Seeger. [S0163-1829(96)09434-9]

I. INTRODUCTION

Cobalt undergoes a martensitic phase transformation from a high-temperature fcc phase into a hcp phase and vice versa around $T_m\approx 693$ K, with some hysteresis of about 20 K. Formally the transformation can be decomposed into a shearing and a sinusoidal relative displacement of atoms. Both the shear and the periodic shuffle displace the closed-packed $(111)_{\text{fcc}}$ planes into a $[11\bar{2}]_{\text{fcc}}$ direction in order to change from a fcc to a hcp stacking. The orientational relationship is then given by $(111)_{\text{fcc}}\|(00.1)_{\text{hcp}}$ and $[11\bar{2}]_{\text{fcc}}\|[1\bar{2}0]_{\text{hcp}}$ or $[\bar{1}10]_{\text{hcp}}\|[\bar{1}10]_{\text{fcc}}$. The transformation temperature as well as the amount and extent are affected by various factors. The fcc phase can be retained by alloying with soluble atoms such as Fe or Ni. Alloying with metallic and nonmetallic elements of a limited solubility range also has a drastic influence on the transformation behavior. It favors the formation of various polytype structures.[1] No influence of magnetism on the martensitic transition has been reported,[2] to our knowledge.

It is suggested in the literature that specific stacking faults might be locally preformed embryolike seeds (''nuclei'') of the phase. The transformation occurs via a two-step nucleation and growth process. Pretransitional phenomena are of key importance for the understanding of a martensitic transformation: An anomalous diffuse scattering was explained in terms of embryonic domains of a premartensitic phase:[3,4] strain-field modulations originating from coherency stresses between mother and daughter phase;[5] nuclei of the daughter phase introducing a strain field in the matrix;[6,7] heterophase fluctuations, creating (metastable) nuclei;[8] and impurity atoms, whose strain fields should act as ''nuclei'' of the transformation.[9] An overview of the different ideas is given by Babkevich, Frey, and Kahlert.[10]

A different approach can be obtained from phonon anomalies. This idea was initiated by a report about an anomalous dip of the Debye-Waller factor around the transition temperature.[11] Krumhansl and Gooding[12] argued that a small decrease of phonon energies, i.e., a small increase of displacements, can trigger off an actual transition. For the fcc-hcp transition in Co, Dmitriev *et al.*[13] and Falkins and Walker[14] proposed a virtual parent phase from which both fcc and hcp phases can be reached via these displacements. Indeed, neutron-scattering experiments[15–17] showed that for fcc-Co transverse shuffle modes of $(111)_{\text{fcc}}$ planes are of low energy. However, in contrast to group-3 and -4 transition metals, where the martensitic bcc-hcp transition are related to phonons of exceptionally low energy,[18] no significant softening of the $T[\xi\xi\xi]$ branch could be observed. Only a step-like decrease of its initial slope some 20° below T_m has been reported.[17] These previous experiments were not fully convincing inasfar as either fcc-Co stabilized by 8 at. % Fe was used,[15,16] or the transformation was approached only from one side (hcp→fcc).[17] Therefore an analogous experiment from above (fcc→hc) has been performed.

A study of the lattice dynamics of the high-T fcc phase seems to be particularly important because the transformation mechanism in both directions cannot be the same: (i) A temperature factor analysis revealed no anomalies in the hcp phase,[19] but an increase of the atomic mean-square amplitudes in the fcc phase if approaching T_m from above. This analysis was, however, affected by possible magnetic contributions to the Bragg intensities which are hard to estimate as the spin structure of Co is not well known in the transformation regime. (ii) The disorder behaviors of hcp and fcc Co differ greatly. (iii) In the hcp phase, small but distinct preformed cubic ''domains'' with a volume ratio of 100:1 (hcp:fcc) exist.[20] These domains only start growing at 20 K below T_m. A sample should be free of these domains to avoid twinning effects. Preferably an experiment should be carried out with a virgin fcc sample which has never been cooled below T_m. A further motivation for a renewed investigation was to look not only for anomalies of the elastic shear constant c_{44} (hcp) or $c' = (c_{11} - c_{12} + c_{44})/3$ (fcc), but also to inspect the lattice dynamics in all main symmetry directions and to look for anomalous shuffle modes.

II. EXPERIMENTAL DETAILS

A Co single crystal was provided by METRONEX, Warsaw, Poland. The mosaic was about 40 min of arc with an indicated purity of 99.9%. To optimize the relatively low coherent scattering (σ=0.80 b) with respect to the high absorption cross section (5.21 b), a sophisticated sample was prepared. Two hollow cylinders were cut by spark erosion with outer diameters of 11 and 14 mm each with a wall thickness of 1.5 mm. Both parts were put on top of one another, preserving a relative orientation of some min of arc and welded in a Nb can to avoid contamination by gaseous impurities (sample 1). The measurements were carried out at the three-axis spectrometer $H8$ at High Flux Beam Reactor at Brookhaven National Laboratories. A PG(002) monochromator, a PG(002) analyzer, a graphite filter behind the sample, and collimations $40'$, $-40'$, $-40'$, $-40'$ were used. A standard resistance furnace was used, providing a stability of ± 1 K and an absolute error ± 3 K. A second experiment was performed on the three axis-spectrometer IN8 of the Institut Laue Langevin with fcc single crystals grown *in situ* (sample 2). This technique has been described elsewhere.[21] Because seeds of the fcc phase are not available, the crystals grown have arbitrary orientations. Most of them have a (110) plane, others (112) and (111) parallel to the scattering plane. In spite of the possibility of tilting the furnace by $\pm 20°$, no (100) orientation could be achieved. To minimize contamination by gaseous impurities, the furnace was evacuated to 10^{-7} mbar for 12 h prior to each crystal growth, and one sample rod was never used more than twice. The Co rod had a nominal purity of $4N8$, the grown crystals a mosaic of typical 30 min of arc. Care was taken not to pass the β-α transition. The inherent drawback of the *in situ* technique is an only crude temperature control. Absolute errors close to T_m and the temperature gradient over the sample are of the order of ± 10 K. A vertical focusing PG(002) monochromator together with horizontal focusing PG(002)/PG(004) analyzers were used in the constant k_f mode. Higher-order contaminations were suppressed by a graphite filter. Due to focusing as well as a proper choice of wavelength and analyzer reflection, no collimators were necessary. In spite of the unfavorable cross sections of Co, phonons could be measured with reasonable statistics within 2 h.

III. RESULTS

Sample 1 was the first to be measured within the stability range of the hcp phase. Between 450 and 650 K, elastic scans along the $(10.\xi)_{hcp}$ rod were performed in order to detect and monitor a minority fcc phase, if any, at positions

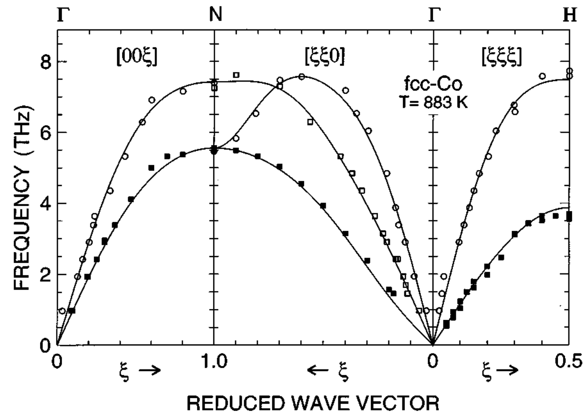

FIG. 1. Dispersion curve of fcc Co measured at 883 K on samples 1 and 2. The solid lines represent a Born–von Kármán fit including interactions up to the fourth-nearest neighbor.

ξ=0.66 and 1.33. Actually two weak peaks were observed at these positions, which showed an almost temperature-independent intensity of roughly 1% when compared to the $(10.1)_{hcp}$ reflection and an intensity ratio of 4:1. Between 700 and 740 K the transformation is completed as monitored by the vanishing $(10.1)_{hcp}$ reflection and a concomitant growth of the fcc precursors. The final volume ratio of both twins remained constant at 4:1. As reported previously,[17] a diffuse rod along $(1.75\ 0.\xi)_{hcp}$ was observed at a temperature close to T_m. No hcp domains survive in the fcc phase at temperatures above the transition hysteresis (cf. Ref. 20). Inelastic measurements in the hcp phase were carried out at 650 K along $T_{[120]}[00\xi]$, in the fcc phase along $T_{[112]}[\xi\xi\xi]$ at 860, 1150, and at 710 K during cooling. At 710 K the initial slope of several dispersion branches were measured in order to determine the elastic constants.

The complete dispersion along the main symmetry directions was measured at 883 K (Fig. 1) by means of several samples 2. A comparison with the dispersions reported earlier[15,16] shows a general agreement, bearing in mind that these measurements were made with fcc-$Co_{92}Fe_8$ at room temperature. Again an eventual temperature dependence of phonon frequencies was tested by measurements of the $T_{[112]}[\xi\xi\xi]_{fcc}$ branch at 1171 and 883 K, and of the equivalent $T_{[120]}[00\xi]_{hcp}$ at 643 and 610 K. Because these crystals have never been transformed through the martensitic transition, they cannot be influenced by any memory effect. In a few cases degeneracy of the $T[\xi\xi\xi]$ branch has been tested, i.e., $T[\xi\xi\xi]$ phonons with [110] polarization have also been measured. No difference could be detected, showing that degeneracy is maintained.

The dispersion has been fitted by means of a generalized Born–von Kármán model with force constants up to the

TABLE I. Elastic constants of fcc-Co (sample 1) and fcc-$Co_{92}Fe_8$ in units of 10^{11} N/m^2.

	Co, T=710 K	$Co_{92}Fe_8$, T=300 K (Ref. 20)	$Co_{92}Fe_8$, T=300 K (Ref. 21)
c_{11}	2.23±0.13	2.21±0.07	2.61
c_{12}	1.86±0.15	1.47±0.15	1.84
c_{44}	1.10±0.04	1.24±0.02	1.22

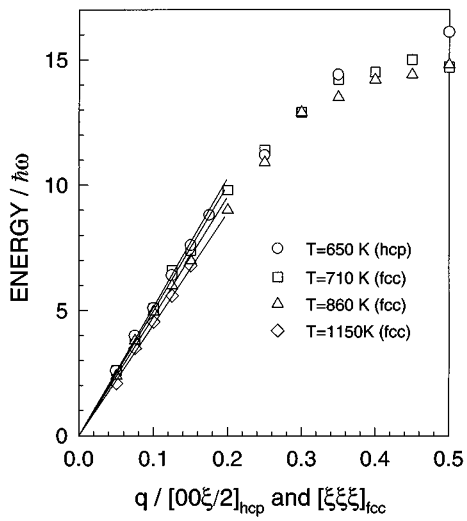

FIG. 2. Dispersion branch $T_{100}[00\xi]_{\rm hcp}$ at 650 K (circle), and $T_{112}[\xi\xi\xi]_{\rm fcc}$, at 710 K (square), 860 K (triangle), and 115 K (cross) (all measured with sample 1).

fourth neighbors. Elastic constants c_{11} and c_{44} were directly determined from the longitudinal and transverse branch along $[\xi 00]$, respectively, and c_{12} can only be evaluated from different branches. Some of the initial slopes cross the steep magnon dispersion.[22] This is of less importance for the phonon branch with the lowest initial slope. Consequently c_{12} has been determined from the $T_{[112]}[\xi\xi\xi]$ branch. For the hcp phase, the corresponding $T_{[120]}[00\xi]$ branch gives direct access to c_{44}(hcp) (Table I). Figure 2 compares the $T[\xi\xi\xi]_{\rm fcc}$ to $T_{[120]}[00\xi]_{\rm hcp}$ branches for all measured temperatures. Both hcp and fcc branches belong to modes with propagation along the stacking direction and polarization vectors perpendicular to it, i.e., parallel to the stacking planes.

Figure 3 shows the temperature dependence of c_{44}(hcp) and c'(fcc), the value of Svensson *et al.*[16] is added. Clearly $c(T)$ can be approximated by a linear behavior either in the

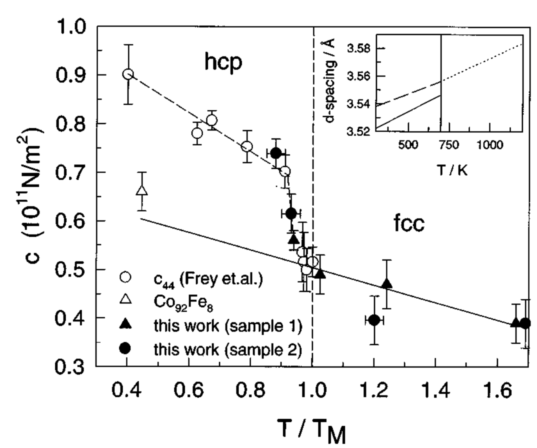

FIG. 3. Temperature dependence of the elastic shear constant c_{44}(hcp) and c'(fcc). Solid triangles: present work (sample 1); solid circles: present work (sample 2); open circles: taken from Ref. 17; and open triangle: taken from Ref. 16 (fcc-$Co_{92}Fe_8$). Lines are only a guide to the eye. Inset: Temperature dependence of the lattice constants redrawn after Ref. 23. Upper line (dashed): $2a_{\rm hcp}$ and $a_{\rm fcc}$ (dotted); lower (solid): $\sqrt{3/2}c_{\rm hcp}$.

hcp or fcc phase, except for an interval of 50 K below T_m. Bolgov, Smirnov, and Finkel[23] reported about the lattice expansion of pure Co up to 1570 K (cf. the inset in Fig. 3). Ideally $a_{\rm fcc}/a_{\rm hcp}=\sqrt{2}$ and $a_{\rm fcc}/c_{\rm hcp}=\sqrt{3/2}$. There is a clear jump of $\sqrt{3/2}a_{\rm hcp}(=a_{\rm fcc})$ at T_m, i.e., the distance of the stacking planes changes by 0.3%. Comparing this to the changes of the elastic constant $\Delta c/c_{44}\simeq 27\%$, it is evident that the latter cannot be explained by any volume change. Rather, it reflects a change in the long-range interaction. However, the decrease of c_{44} some 50 K below T_m cannot be understood in this way. Moreover, the cubic precursors start to grow only 20 K below T_m, where the transformation is complete. At T_m below 50 K, the intensity of the fcc precursor is still unchanged compared to the value at 450 K. Therefore, there are several arguments for a real anomaly in the behavior of c_{44} in a 50 K interval below T_m. As found earlier with the same sample material,[19] the back transformation fcc→hcp starts at 668 K, i.e., the measurement at 710 K was definite in the fcc phase.

IV. DISCUSSION

Two similar Ginsburg-Landau expansions for the reconstructive fcc-hcp transition have been proposed. Dmitriev *et al.*[13] interpreted the two phases as differently ordered structures of a common disordered hexagonal latent parent phase, whereas Falkins and Walker[14] propose a common simple hexagonal parent phase, from which fcc or hcp are formed by a simple shear or modulated shuffle of neighboring basal planes in the $[112]_{\rm fcc}$ or $[120]_{\rm hcp}$ direction. In both approaches symmetry considerations lead to strong constraints on the proposed order parameter. For instance, Dmitriev *et al.*[13] predicted that longitudinal and transverse phonon dispersions along the high-symmetry directions $[\xi\xi\xi]_{\rm fcc}$ and $[0\xi\xi]_{\rm fcc}$ do not change when transforming from fcc to hcp. Falkin and Walker[14] proposed a transition trajectory along the Shoji-Nishiyama transition, i.e., they explicitly foresaw low displacement barriers for a shear and modulated shuffle of (111) planes along $[112]_{\rm fcc}$.

Our results and previous work on fcc-$Co_{92}Fe_8$ (Refs. 15 and 16) and hcp-Co (Ref. 17) confirm the low energy of the $T[\xi\xi\xi]$ phonon branch, and therefore indicate low potential barriers for displacements along the basal planes. However, they also confirm with great precision the absence of any anomaly in the $T[\xi\xi\xi]$ phonon branch, for instance at $\xi=1/6$ or 1/3 (cf. Ref. 15). Further, the $T[\xi\xi\xi]$ dispersion shows no decrease in frequency when approaching the phase transition from above, i.e., no soft mode behavior, confirming Dmitriev *et al.*'s statement.[13] We cannot confirm, however, that the "hexagonal" and "cubic" branches along Γ-K-M coincide when approaching the transformation regime, as suggested by Dmitriev *et al.*

The difference in the absolute values of $c_{44}(T)_{\rm fcc}$ reflects a change in the long-range interaction of the stacking planes. The most significant feature remains the fact that the decrease of c_{44}(hcp) occurs 50 K below T_m, which is fairly far from the onset of the hcp-fcc transition. No anomalies of c' are observed in the fcc phase. The stacking disorder, the existence of elastic precursor signals, and the c_{44} anomaly occur only in the low-T hcp phase.

We interpret our observations on the basis of Seeger's model,[24,25] where the nuclei of the hcp to fcc and fcc to hcp transformations are special dislocation arrangements. The essential point is the onset of the motion of dislocations triggered by suitable phonon modes, in our case shear modes. As outlined by Flytzanis, Crowley, and Celli,[26] the mobility of screw dislocations may be triggered by phonons, and the coupled dislocation-phonon complex moves in a solitonlike mode through the (nonlinear) medium. Clearly, the special dislocation configuration is not a ''normal'' fault. Therefore, the faults in the hcp phase, as manifested by the diffuse rods, are not responsible for the transformation. This faulting is most likely due to frozen dislocations. In this picture, stacking faults in the hcp phase and also the fcc remainders are a byproduct of the fcc to hcp transformation. In the reverse direction, the kinetics is not hindered; faults and ''wrong'' stacking sequences can ''anneal.'' Nevertheless, the rare dislocation configuration, which carries the transformation, must survive, and can be activated by a renewed cycling. The dependence of T_m on particle size may be understood by a hindering of the mobility of the ''complex'' by surface effects. In very small particles the special configuration might be absent, and no transformation of the virgin fcc phase takes place. Summarizing, different phenomena may be explained with Seeger's model, but no direct proof is given.

V. CONCLUSIONS

Neither dynamical nor static anomalies were found in the high-temperature fcc phase of pure Co. It might be concluded that the martensitic phase transition between fcc and hcp is less affected by phonon anomalies, and that excess entropy caused by low-energy modes in the high-temperature phase is less important. The extreme sensitivity of the phase transition on impurities leads us to the conclusion that lattice defects play an important role. A dislocation-driven transformation mechanism proposed by Seeger reconciles our experimental findings. However, to our knowledge, the coupling and interaction between phonon modes and the mobile dislocation is still a field not well investigated so far. From the thermodynamic point of view, electronic and magnetic properties of Co might play an important role in stabilizing the high-temperature phase, which is beyond the scope of this paper.

ACKNOWLEDGMENTS

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