

Disorder in Cobalt Single Crystals

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(Received 27 February 1981; accepted 15 April 1981)

In honour of Professor Dr H. Jagodzinski's 65th birthday

Abstract

Disorder in both allotropic phases of pure single-crystalline cobalt was studied by elastic neutron scattering in order to separate bulk from surface effects and to remove diffuse inelastic contributions. The intensity variation along $10l$, measured at different temperatures, was analysed quantitatively in terms of Jagodzinski's disorder theory. The values found for the degree of disorder in the h.c.p. phase were lower than those reported before for powder samples and remain nearly unaffected when approaching the transition temperature. The f.c.c. phase is always (below and above the transition) well ordered. However, the temperature behaviour of the f.c.c. and the h.c.p. precursor regimes in the h.c.p. and the f.c.c. modifications, respectively, is different. The connection between disorder and the martensitic h.c.p.–f.c.c. transformation is discussed.

I. Introduction

Pure single-crystalline cobalt exists in two close-packed modifications: the h.c.p. form is stable below $T_m \sim 700$ K and transforms into the f.c.c. modification above T_m . There are some controversial findings about an additional transformation from the f.c.c. again into the h.c.p. phase by passing the Curie temperature $T_c = 1394$ K (*Cobalt Monograph*, 1960). This point is not considered in this paper. Owing to the geometrical similarity of the two types (the c/a ratio of 1.623 is nearly the ideal value $\sqrt{8/3}$), a small volume change of 0.2%, the same coordination of the next-nearest neighbours, and a small difference of about $420 \text{ J (g atom)}^{-1}$ in the free energies of the two forms (*Cobalt Monograph*, 1960), a mixing of the two phases, *i.e.* an intergrowth of h.c.p. and f.c.c., as well as disorder phenomena concerning irregularities in the correct sequences of close-packed layers, was observed. The extent to which these phenomena occur is known to be heavily influenced by the thermal history, the purity – particularly alloying with Fe – the grain size and the actual values of temperature and pressure (Schumann,

1969). Most investigations were hitherto carried out on powder specimens with various degrees of particle size. However, with respect to the detailed theoretical considerations on one-dimensional disorder it is surprising that only a few *quantitative* measurements on single crystals of Co were carried out (Kajiwara, 1970; Creagh, Bailey & Wilson, 1975). To the knowledge of the authors no such diffraction experiments with X-rays or neutrons are reported. As emphasized by Houska, Averbach & Cohen (1960) results obtained on powder samples do not necessarily apply to the bulk single crystal where surface and size effects are *not* the dominating factors.

We performed elastic neutron measurements mainly for two reasons: to remove the diffuse inelastic contributions to the disorder scattering – which is important for a quantitative analysis – and, secondly, to separate bulk from surface effects. By these measurements we wanted to determine the exact degree of disorder in both modifications and its variation as a function of temperature. The last point was suspected to be connected with the h.c.p.–f.c.c. transformation mechanism which is martensitic, that means, of strongly first order. Together with results obtained earlier from inelastic neutron investigations (Frey, Prandl, Schneider, Zeyen & Ziebeck, 1979), this should shed some light on the microscopic origin of a martensitic transformation.

II. One-dimensional disorder

Stacking disorder in Co is due to irregular sequences of the hexagonal close-packed layers along the hexagonal [001] or one of the cubic $\langle 111 \rangle$ directions. With the *ABC* notation for the two close-packed arrangements, perfect ordering as well as the various types of faults in the stacking sequence can easily be seen from a projection on a hexagonal $\{110\}$ or a cubic $\{112\}$ plane. In Fig. 1 the well known facts are summarized. Any interruption in the correct (h.c.p. or f.c.c.) sequences produces a regime belonging to the other allotropic type. A deformation- (= slip- = transformation-) type fault can be created either by a real

providing an 'elastic window' of ± 0.5 THz. The $\lambda/2$ contamination within the monochromatic beam was about 0.5%. The resolution of the instrument was better than $1/100a^*, b^*, c^*$, the furnace/supply equipment was stable to within ± 1 K. Scans were registered mostly along $10l$ at different temperatures up to 770 K. Both samples were cycled a few times through the h.c.p. \leftrightarrow f.c.c. transition. Except for different volume ratios of twins (created during the transformation f.c.c. \rightarrow h.c.p.) and a different transformation temperature T_m (~ 678 K for sample 1 and ~ 707 K for sample 2), which is quite normal for this type of transformation, no different behaviour for the various equivalent scans and for the different crystals under investigation could be detected.

The measured profiles were corrected for spurious and incoherent background contributions. Fig. 2 shows the integral and purely elastic scans along $10l$ at room temperature. The diffuse intensity is mainly of elastic origin. This also holds for the measurements at higher temperatures. Only the elastic data were used in the quantitative evaluations. Here instrumental broadening can be neglected (as calculated from the resolution function) with the exception of the data measured close to the cubic $l = \frac{2}{3}$ and $\frac{4}{3}$ positions above T_m (see below).

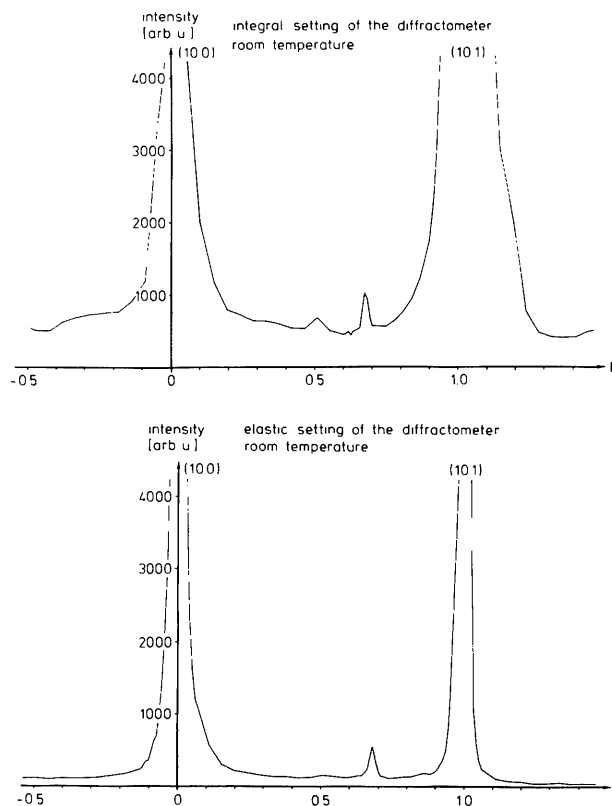


Fig. 2. Integral and purely elastic scans along $(10, l)$ at room temperature. The broadening of the integral profiles is due to instrumental resolution effects. (The term 'integral' is used for measurements without an analyser.)

The ratios of the integral breadths (defined by Wilson, 1942) of the reflections 100 and 101 are 2.63 ± 0.49 and 2.38 ± 0.51 for the two samples, *i.e.* close to 3. The width of the streak measured perpendicular to c^* is comparable with that of the Bragg peaks, independent of any temperature variation. The intensity ratio of diffuse elastic to Bragg scattering is of the order of 10^{-3} . Even at room temperature very weak but sharp cubic reflections exist in a sample not cycled through the transition point T_m (*cf.* Fig. 2). By comparing the Bragg intensities a volume ratio h.c.p.:f.c.c. of 100:1 at room temperature can be estimated. The width of the cubic reflections along c^* corresponds to the instrumental resolution from which an extension of the cubic stacking sequences of at least 100 layers or 200 Å (= 20 nm) can be estimated. Two cubic twins can be observed at positions $l = \frac{2}{3}$ and $\frac{4}{3}$, respectively. In each of the investigated samples only one of them is appreciable, the other one being extremely weak. The hexagonal, the cubic and the diffuse intensities remain nearly constant up to about 680 K. Some 20 K below T_m the cubic reflections start to grow remarkably (Fig. 3), while the intensity of the hexagonal ones falls by roughly 40%. After passing the transition point – detectable by a rapid decrease of the hexagonal Bragg intensities – very diffuse peaks are still observable at the hexagonal positions some ten degrees above T_m . At 40 K above T_m no intensity apart from the background could be observed at $l = 0$ and $l = 1$. The new strong cubic reflections remain sharp, no diffuse intensity modulation along l is observed.

The degree of the disorder of the hexagonal and the cubic modifications, either as parent or as precursor phase, will be discussed in the following section. By means of a quantitative comparison of the overall elastic intensity distribution with an appropriate disorder theory the exact probabilities for disordering and its

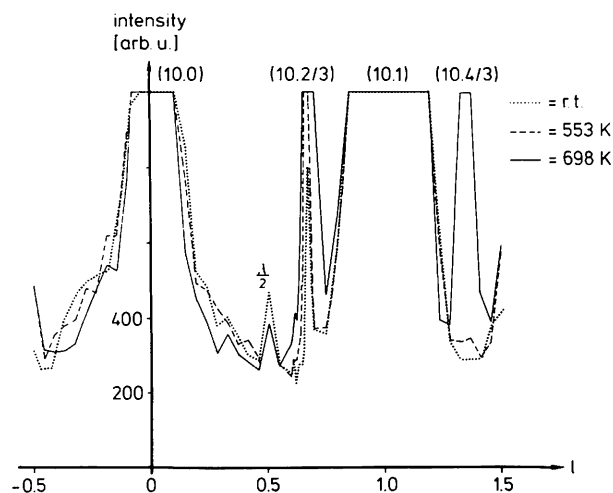


Fig. 3. Integral scans along $(10, l)$ at different temperatures. The growth of the cubic nuclei below the transition temperature is clearly visible.

variation with temperature can be calculated. Moreover, it can be decided whether or not disorder phenomena in Co are correlated with the martensitic transformation mechanism itself.

IV. Comparison with Jagodzinski's disorder theory

Jagodzinski introduced in his disorder theory interactions up to three layers ($s = 3$) accounting for higher periodic sequences in close-packed lattices. We use the symbols α for the probability of a mistake in the fourth layer of a h.c.p. sequence and $(1 - \beta)$ for the equivalent probability of an interruption in a f.c.c. sequence, limiting cases result for $\alpha \rightarrow 0, \beta \rightarrow 0$ (h.c.p.); $\alpha \rightarrow 1, \beta \rightarrow 1$ (f.c.c.) and $\alpha \rightarrow 0, \beta \rightarrow 1$ (coexisting disordered h.c.p. and f.c.c. sequences). The probability of finding the same layer as the reference layer in a distance of m layers is given by $P_m = K_0 + \sum_{v=1}^4 K_v x_v^m$, where K_v and x_v are functions of α and β . The x_v are to be calculated from a characteristic equation, the K_v from the boundary conditions [Jagodzinski, 1949*b*; equations (10) and (21*b*)]. The fundamental intensity equation given by Wilson (1942)

$$I_{\text{diff}} = \sum_{m=-(N_3-1)}^{+(N_3-1)} (N_3 - |m|) \langle F_j F_{j+m}^* \rangle e^{2\pi i m l}$$

($h - k = 3n \pm 1$, $n = \text{integer}$), l is a continuous parameter, can be written as a function of the above parameters:

$$I_{\text{diff}} \simeq N_3 |F|^2 \sum_{v=1}^4 \frac{K_v (1 - x_v^2)}{1 - 2x_v \cos 2\pi l + x_v^2}. \quad (1)$$

Because x_3, x_4 and K_3, K_4 are complex conjugate,

$$x_3 = \rho e^{i\varphi}; \quad x_4 = \rho e^{-i\varphi};$$

$$K_3 = A + iB; \quad K_4 = A - iB,$$

(1) can be expressed in the following form:

$$I_{\text{diff}} \simeq N_3 |F|^2 \left\{ \frac{K_1(1 - x_1^2)}{1 - 2x_1 \cos 2\pi l + x_1^2} + \frac{K_2(1 - x_2^2)}{1 - 2x_2 \cos 2\pi l + x_2^2} + \frac{A(1 - \rho^2)}{1 - 2\rho \cos(2\pi l - \varphi) + \rho^2} + \frac{A'(1 - \rho^2)}{1 - 2\rho \cos(2\pi l + \varphi) + \rho^2} - 4B\rho \sin \varphi [(1 + \rho^2) \cos 2\pi l - 2\rho \cos \varphi] \times \{ [1 - 2\rho \cos(2\pi l - \varphi) + \rho^2] \times [1 - 2\rho \cos(2\pi l + \varphi) + \rho^2] \}^{-1} \right\} \quad (2)$$

($A \neq A'$, see below), where F denotes the structure factor of a layer and N_3 the number of layers along the hexagonal c axis.

The first four terms describe more or less diffuse peaks at positions $l = 0, 1, +\varphi/2\pi, -\varphi/2\pi$, whose widths are determined by x_1, x_2 and ρ .

The last term yields an asymmetric contribution which is negligible in the case of Co. The corrected experimental data were fitted to (2) giving parameters $K_1, K_2, x_1, x_2, A, A', \rho$ and φ . The last parameter φ was found to be close to $120^\circ (\pm 0.5^\circ)$, independent of the temperature corresponding to cubic sequences. K_1, K_2, A, A' were taken as free parameters, thus allowing for different grains with different values of N_3 as would be the case for mainly hexagonal regimes and mainly cubic twins and nuclei in the specimen. From (10) (Jagodzinski, 1949*b*), one derives four equations coupling α and β with x_1, x_2, ρ and φ . Since φ is determined only within $\pm 0.5^\circ$ and on the other hand is very sensitive to α and β , it was eliminated from these equations. Moreover, one has to consider an incongruent intergrowth of small 'cubic' grains with the 'hexagonal' ones. Therefore, φ and also ρ might be in error for the determinations of α and β for the 'hexagonal' grains. Eliminating also ρ leaves us with two equations from which α and β can be determined, with the measured values of x_1 and x_2 only. In this procedure it turns out that α is generally very well determined ($\pm 0.2\%$), while β , which comes out to be between 0 and 15%, is practically underdetermined ($\pm 50\%$). On the other hand, from the values of ρ and φ the probabilities α and β for faults within the 'cubic' grains can be determined: with $\varphi \simeq 120^\circ$ we obtain good values for β , while α is now totally undetermined ($\simeq 90\% \pm 100\%$). Fig. 4 shows the experimental data together with the fitted profiles for the two samples and for the different temperatures. A logarithmic scale was chosen in order to emphasize the wings of the peaks which are most important for disorder scattering. The overall agreement is remarkably good for $T < T_m$. Above T_m it was not possible to fit the measured profiles with (2). However, in the derivation of (2) terms of the form

$$2K_v \{ 2x_v^2 - x_v(1 + x_v^2) \cos 2\pi l + x_v^{N_3+1} \cos 2\pi l(N_3 + 1) - 2x_v^{N_3+2} \cos N_3 2\pi l + x_v^{N_3+1} \cos(N_3 - 1)2\pi l \} \times (1 - 2x_v \cos 2\pi l + x_v^2)^{-2} \quad (3)$$

were neglected because they are small for large N_3 [Jagodzinski, 1949*b*, equation (22)]. Consequently, the broad peaks at the hexagonal positions above T_m suggest that N_3 (hexagonal) is not large. Indeed, adding the terms (3) in (2) ['modified equation (2)'] yields a reasonable fit for the 'hexagonal' peaks. From this, values for N_3 were determined in sample 1: $N_3 = 39 \pm 7$ at $T = 698$ K, 35 ± 5 at $T = 728$ K; sample 2: $N_3 = 25 \pm 3$ at $T = 717$ K, whereas at $T = 758$ K practically

no 'hexagonal intensity' could be detected. The agreement of the fits with the modified equation (2) for the 'cubic' peaks is worse, because the interferences are so narrow that instrumental resolution effects should have been included. No such attempts have been made because these peaks are further influenced by extinction.

The probabilities α (hexagonal) and β (cubic) are plotted as functions of temperature in Fig. 5. Both values remain almost constant over the whole temperature regime. The small increase of α above T_m (which is, however, within the e.s.d.) may be explained by the small particles: considering the boundary layers of a particle as a fault, the probabilities at $T = 698$, $T =$

728 (sample 1) and $T = 717$ K (sample 2) are $\alpha \gtrsim 5, 6$ and 8%, respectively, in gross agreement with the observed values. Thus it may be concluded that the probability α 'inside' the domains stays constant also above T_m . The same holds for β (cubic) below T_m , for which a slight decrease might be suspected (see Fig. 5). The variation of the relative intensities of the 'hexagonal' and 'cubic' peaks thus can only be explained by a variation of the values of N_3 , i.e. hexagonal and cubic regimes exist together and start to grow or diminish when the temperature is changed. A further indication for the conclusion of unchanged values α and β are the constant values for the coefficients K_v [see equation (2)].

In the single crystals of Co investigated, the hexagonal and the cubic modification always coexist at temperatures below T_m . Both phases are disordered only by a small amount, roughly 2.5% for the h.c.p. and 0.5% for the f.c.c. regimes. It is remarkable that the f.c.c. arrangements are realized in the state of long-range order with a low density of stacking faults within the stable h.c.p. mother phase. These cubic stacking sequences are extended along the stacking direction beyond 100 layers. By the ratio of the integral breadths of the hexagonal 100 and 101 reflections we conclude that the faults are mainly of the growth type. These results are hardly comparable with findings by powder investigations (Edwards & Lipson, 1942; Paterson, 1952; Anantharaman & Christian, 1956; Houska, Averbach & Cohen, 1960; Toth, Day, La Force & Ravitz, 1964; Creagh, Bailey & Wilson, 1975) where both - deformation and growth - faults in the h.c.p. phase were found. Moreover, there the probabilities for the density of faults vary considerably due to

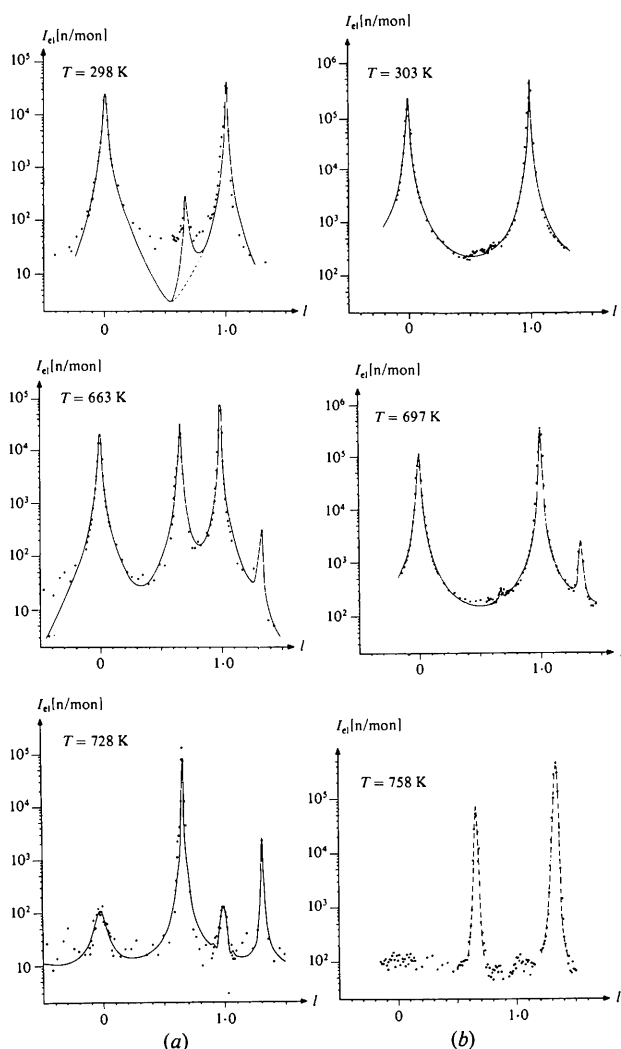


Fig. 4. Elastic scans along (10.l) at different temperatures together with the fitted profiles for the two sample crystals. (a) Sample 1; (b) sample 2. The fits are according to equation (2) except for the data at $T = 728$ K (sample 1) and $T = 758$ K (sample 2). In the former case the fit is according to the modified equation (2) (see text), in the latter case only two single Gaussian profiles are used. Note the different behaviour of the cubic twins in the two samples.

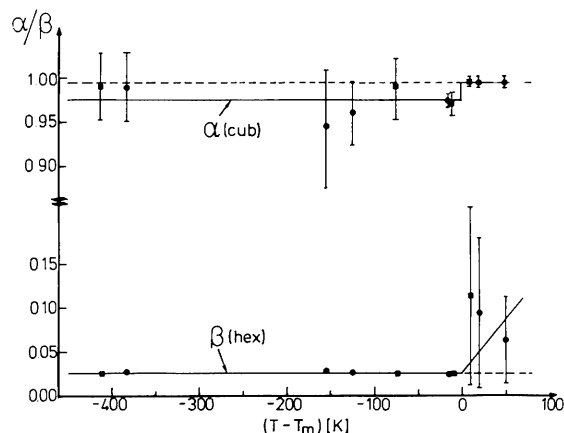


Fig. 5. Probability for a cubic sequence, if the foregoing three layers are hexagonal (α) or cubic (β) for sample 1 (●) and sample 2 (■) as a function of the temperature difference from the transition temperature T_m . Where error bars are omitted, the error is smaller than the symbol. The probabilities relate to hexagonal (α) and cubic (β) grains; see text. The solid and dashed lines for α above T_m and β below T_m are only speculative (see text).

a different prehistory, state and kind of sample. The absolute values are generally higher than ours, a comparable value of 7% was found by Creagh *et al.* (1975) in the h.c.p. phase. This might be due to a misinterpretation of TDS or due to a different state of order of the smaller 'X-ray crystals'. Furthermore, the density of faults varies not only from sample to sample, but also from grain to grain in one powder specimen (Toth *et al.*, 1964). Concerning the existence of the f.c.c. precursor phase below T_m , Houska *et al.* (1960) and Creagh *et al.* (1975) report an almost perfect ordering in full accordance with our results.

The stacking faults within the hexagonal modification are not in thermodynamic balance, as no reversible change of the stacking fault width in the layer plane with the temperature could be detected. Because the volume ratio hexagonal/cubic below T_m amounts to about 100:1 and one cubic nucleus extends over more than 100 layers, the thickness of the hexagonal sequences corresponds to more than 10^4 layers. Assuming a uniform distribution of faults a probability of a mistake of 2.5% indicates an interruption in the stacking sequence after about 40 steps. If such faults were responsible for the formation of extended cubic sequences, only every 250th fault would be effective. For such behaviour there is no clear indication. On the other hand, because the value of 2.5% represents an average over the whole volume, statistical fluctuations might lead to an accumulation of faults which itself could serve as the nuclei for the extended cubic sequences. In this case the thickness of the hexagonal layer packets could not be estimated.

However, in the temperature regime below T_m , where the f.c.c. nuclei start to grow considerably, the degree of disorder in the h.c.p. phase remains unaltered, *i.e.* the stacking disorder remains unaffected, which is difficult to understand in the accumulation concept. Therefore the stacking faults cannot be responsible for the transformation h.c.p. \rightarrow f.c.c. This is also plausible because of the narrow similarity of the geometric arrangements and the specific volume in both modifications of Co; a simple stacking misfit represents no serious interruption.

Internal interfaces like incoherent grain boundaries or twin boundaries or special dislocation arrangements probably play a decisive role for the formation of the (cubic) nuclei and the state of order within the nuclei. The existence of such internal interfaces or defect arrangements is normal in a crystal which undergoes a martensitic type of transformation. Consequently, stresses and strains have the most important influence on the transition behaviour and on the state of order below T_m .

At this stage of the discussion it should be emphasized that no distinction can be made in our experiment between a true stable or only a metastable state of the daughter f.c.c. phase. A metastable state

could be formed either during the sample crystal's growth process by the formation of energy barriers preventing the full transformation f.c.c. \rightarrow h.c.p. (crystals are grown from the melt, *i.e.* every crystal was in the f.c.c. phase before!) or by low-frequency heterophase fluctuations (Cook, 1975). In the latter case quasielastic scattering around $10\frac{1}{2}$ should occur which in the present experiment is hidden in the energy resolution of the instrument.

The situation above T_m obviously is different. The f.c.c. modification is now the stable phase and h.c.p. sequences – if any – could play the same role as the f.c.c. nuclei below T_m . But some ten degrees above T_m only small hexagonally ordered layer packets exist which vanish completely with an increase of temperature. Another explanation for the broad diffuse peaks at the hexagonal positions would be a kind of short-range order of *ABAB* sequences within the cubic phase which seems, however, unlikely in comparison with the former interpretation. In any case, in contrast to the f.c.c. nuclei below T_m , no h.c.p. nuclei can be responsible for the back transformation f.c.c. \rightarrow h.c.p. The cubic phase above T_m is, within the limits of our experimental resolution, again well ordered. Single planar or linear defects of another kind are not visible in this conventional type of a scattering experiment. Nevertheless, there must be some kind of memory effect within the f.c.c. regimes for the back transformation. This can be concluded from the fact that in one sample the cubic twin corresponding to the $l = \frac{2}{3}$ position in reciprocal space dominates after repeated cycling across T_m , in the second sample the other twin ($l = \frac{4}{3}$) plays an analogous role.

We conclude from these experimental findings that the degree of stacking disorder is not correlated with the transformation. The transition mechanism is, however, coupled with other types of faults which are less frequent than stacking faults. A more detailed discussion is given in the next section.

The existence of only *growth* faults within the h.c.p. modification can be understood from the fact that deformation faults, possibly formed during the growth process, are easily removed by gliding half-dislocations of the Shockley type along the basal plane (see, for example, Weertman & Weertman, 1964).

V. Allotropic transformation

As discussed in the previous section, the origin of the h.c.p. \rightarrow f.c.c. transition is restricted to a few cubic nuclei which are preformed below T_m . The phase transition corresponds to a nucleus growth and not to a nucleus formation process. These nuclei are well ordered packets of at least 100 layers with the *ABC* sequence. Because the difference in the free energies is relatively small, the nucleus growth process is coupled

with strains. These strains are not likely to be due to the stacking faults in the hexagonal AB sequence (sharp $00l$ reflections!), but are probably due to incoherent interfaces or other defect aggregations. The transformation mechanism can be thought of as a simple shear parallel to the basal plane where the dislocation lines with Burgers vector $\mathbf{b} = [\bar{2}10]$ can glide easily. Approaching the transition temperature, strains can be diminished. Possibly this dislocation mechanism will be triggered by an elastic shear weave which shows an anomalous temperature behaviour in the critical region (Frey *et al.*, 1979).

For the back transformation f.c.c. \rightarrow h.c.p. a different picture seems to be responsible, as no preformed hexagonal nuclei exist above T_m . Additionally, the transposition mechanism must be more complex for achieving the correct ... $ABAB$... stacking starting from the cubic ABC stacking. Seeger (1953, 1956) proposed a model for the transition where a special dislocation arrangement of two pole and two Shockley half-dislocations are combined. The running half-dislocations on a helix-like plane around the $[111]$ pole line perform the transition. In this model the defect configuration corresponds to a 'nucleus' for the new hexagonal phase, its 'growth' is the Seeger mechanism, which can also be thought to be a migration of interfaces between the old (f.c.c.) and the new (h.c.p.) phase. The hysteresis effect is explained within the frame of this model by a hindrance of the movement of the partials caused by repulsive forces between these dislocations after performing one (or a few) turn(s) around the pole dislocation.

Because these 'nuclei' are fixed within the f.c.c. matrix the crystal may exhibit a memory effect. A growing together of different hexagonal grains produces either stacking faults of any kind or grain boundaries if the pole dislocations belong to different cubic $\langle 111 \rangle$ directions. Seeger suggests that the special dislocation arrangement is not too frequent and could therefore be absent in very small grains. This is one explanation for the observation of a pure f.c.c. phase at room temperature when using finely powdered samples. In another explanation, by Knapp & Dehlinger (1956), a strong hindrance of the running dislocations is supposed either by grain boundaries or by interfaces or surfaces which prevent the full back transformation f.c.c. \rightarrow h.c.p.

In a single crystal, however, the f.c.c. \rightarrow h.c.p. transformation should be complete, disregarding the unavoidable twinning (at normal pressure conditions). Cubic sequences may survive when the shear mechanism is stopped by internal interfaces, dislocation nodes, *etc.*

However, while our experimental findings give direct evidence for the above picture of the h.c.p. \rightarrow f.c.c. transformation, they are not inconsistent with Seeger's model for the f.c.c. \rightarrow h.c.p. back transformation. The

nucleus growth processes agree with the martensitic character as a diffuseless and rapid transformation. Thermal activation could enable an overcoming of energy barriers during the transition processes. However, the formation of the nuclei are not thermally activated but coupled with special static defects within either modification of Co.

VI. Conclusions

The quantitative measurement of both diffuse and sharp interferences in a small section of the reciprocal space of cobalt, carried out at different temperatures in the hexagonal and in the cubic modification, allows for a simultaneous study of order phenomena and of the behaviour of a crystal transforming martensitically. The amount of stacking disorder in the h.c.p. modification is small in a single crystal and scarcely influenced by the allotropic transformation, since it is temperature independent and also unaffected by cycling the sample through the transition point. On the other hand, defects other than stacking faults are important for the forward and backward transformation. This situation is dissimilar to transitions in compounds (like SiC) where an equivalent allotropic transformation of first order is accompanied by extensive disordering and even with the formation of polytype structures. The martensitic transition in cobalt in both directions is a heterogeneous process, where a nucleus growth represents the transformation mechanism. Nuclei are either preformed regimes of the daughter phase or special defect arrangements.

Unfortunately, there exist only a few detailed investigations concerning martensitic transformation mechanisms. This is mainly due to experimental difficulties when observing phase transitions of a strong first order: a challenge for future experimental work.

The support and advice of Dr Zeyen during the experiments on the HFR/ILL Grenoble is gratefully acknowledged. The work was supported by funds of the BMFT (project 03-45 E 12).

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Acta Cryst. (1981). **A37**, 826–837

X-ray Study of the Charge Distribution in MgF₂

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(Received 9 July 1980; accepted 21 April 1981)

Abstract

X-ray structure factors of MgF₂ were derived from accurate measurement of single-crystal diffraction intensities. The crystal charge density was analyzed in terms of multipole expansions centered at the ionic sites. Separation of electronic and dynamic deformations was effected by using, in the difference series calculations, anisotropic Debye–Waller factors obtained in the neutron diffraction study of Vidal-Valat, Vidal, Zeyen & Kurki-Suonio [*Acta Cryst.*

(1979), **B35**, 1584–1590]. The charge density was found to be composed of well defined local Mg²⁺ ions and slightly enlarged and more diffuse F⁻ ions with 0.50 electrons distributed more widely in the unit cell. Nonspherical deformations of electronic origin were found significant up to fourth order, with the exception of the vanishing dipole moment of fluorine. These deformations emphasize the ionic nature of the crystal by violating the symmetry of the immediate surroundings and by decreasing the charge density in all of the octahedral bonding directions of Mg²⁺ down to typical ionic values.