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Cubic and hexagonal single-crystal elastic constants of a cobalt-nickel alloy*

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A cubic single crystal of cobalt–32-wt% nickel was transformed to a hexagonal single crystal by cooling a uniaxially prestressed specimen. Evidence that the transformed specimen is a hexagonal single crystal was obtained by Laue x-ray photographs, surface markings, analysis of the magnitude of sound-wave velocities and the symmetry of their polarizations, and the magnetic field dependence of the attenuation of certain modes. The complete sets of second-order and third-order elastic constants of both the cubic and hexagonal phases were measured. These constants were used to calculate the change in enthalpy upon transformation, and the stacking-fault energy. The results are in good agreement with available thermodynamic data.

I. INTRODUCTION

Solid-state phase transitions are often accompanied by significant changes in many physical properties of the polymorphic material. The elastic properties, in particular, are highly dependent upon the crystal structure and crystal-structure transitions generally cause noticeable changes in the elastic constants.

Elastic constants are among the most accurately measurable experimental quantities. However, until recently, elastic constants of both phases of a polymorphic substance had not been measured. The measurements of the complete set of elastic constants requires a single crystal and single crystals of sufficient size of both phases of a substance have not previously been available. If the complete sets of elastic constants of both phases are known, the Debye temperatures can be calculated and used to give a simple description of many thermodynamic properties of the phase transition, such as the enthalpy change upon transformation.

The cobalt-nickel alloy system was selected for study. At high temperatures, these alloys form a continuous face-centered-cubic (fcc) solid solution. Cobalt-nickel alloys are reported to have neither long-range nor short-range ordering.[1] These observations are expected since nickel and cobalt have similar physical, chemical, and electronic properties.[2] In cobalt-rich alloys, a phase transition occurs at lower temperatures to a hexagonal close-packed (hcp) crystal structure. In pure cobalt, the fcc-hcp transition temperature is about 420° C.[3] The transition occurs at lower temperatures for higher nickel content alloys and near room temperature for alloys near 30-wt% nickel.[4]

Because of hysteresis, a cobalt-nickel alloy can be chosen with a starting temperature of martensite formation (M_s) below room temperature and a starting temperature of austenite formation (A_s) above room temperature. (The M_s and A_s temperatures are, respectively, the temperatures at which martensite begins to form during cooling and at which austenite begins to form during heating.) Thus, both crystal structures of such an alloy can be obtained at room temperature.

Phase-transformation studies on cobalt-nickel alloys have been made by deLamotte and Altstetter,[2] Adams and Altstetter,[5] and Rashid and Altstetter.[6] They have been successful in transforming small cubic single crystals to hexagonal single crystals.

In Sec. II, we describe a procedure for effecting the cubic-hexagonal single-crystal transformation, and report the second- and third-order elastic constants of both structures. In Sec. III, we briefly discuss the symmetry of the elastic constants and the Cauchy relations. In Sec. IV, the elastic-constant data are used to describe thermodynamic properties of the phase transition.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Single-crystal transformation and crystal preparation

Two single crystals of cobalt-nickel were obtained from Monocrystals Co. (Cleveland, Ohio). Since the transition temperature is very sensitive to nickel concentration,[4] several attempts to grow crystals resulted in ingots that were partially transformed at room temperature. Ingots were grown that contained single crystals that were sufficiently large for present needs. Both crystals were in the high-temperature fcc phase.

Sections of each ingot were analyzed for nickel and impurity concentrations. Both ingots contained (31.8 ± 1.0)-wt% nickel. The only impurities detected were calcium (200 ppm), iron (500 ppm), and carbon (5 ppm).

One crystal was prepared directly for cubic elastic-constant measurements; the second crystal was prepared for transformation to the hcp phase. The second crystal, when transformed, was to be used for the hcp elastic-constant measurements. The method of transforming the crystal closely followed the procedures of deLamotte and Altstetter.[2]

DeLamotte and Altstetter[2] found that specimens that were transformed either under no external stress or under stresses below the plastic range were always multivariant; that is, all four {111} planes occurred as habit planes. Specimens prestressed plastically but transformed under either small elastic loads or under no load transformed univariantly; the (111) slip plane was the only habit plane. Their findings indicate that prior slip is more important than stress in determining the habit-plane variant. They also found that the amount of hcp phase formed on cooling increased with external stress and that no cubic phase was observed by x-ray diffraction or by other means after prestressing the specimen plastically and cooling to 120 °C.

The M_s temperature determined for the present alloy was about $-10\,^\circ$C, close to the M_s temperature reported by deLamotte and Altstetter for an alloy of slightly lower reported nickel content. The A_s temperature reported by deLamotte and Altstetter is about 100 °C, while Rashid and Altstetter[6] reported 110 °C for an alloy of the same nominal composition. The M_s temperature was determined in this work by slowly cooling small specimens and noting the temperature at which transformation markings first appeared on a prepolished surface. These transformation markings are bands and fine striae that form on the surface of the specimen. They have been shown to be traces of the habit planes.[2]

The crystal to be used for cubic measurements was a cube with (001), (110), and ($\bar{1}$10) faces. This crystal was etched in a solution of two parts phosphoric acid and three parts 30% hydrogen peroxide to remove the machining damage. Laue back-reflection photographs showed the misorientations to be less than 0.5°. Opposite faces were polished flat and parallel to ±100 μin. The dimensions of the crystal were about 11×15×16 mm. The density of crystal 1 was found to be 8.8154 ± 0.001 g/cm^3.

The second crystal was cylindrical in shape with a diameter of 31 mm and a length of about 22 mm. It was also etched, and Laue back-reflection photographs were used to determine the orientation of the cylinder axis, which was found to be close to [249]. No grain boundaries were detected by either Laue photographs or by the etchant. When stressed axially, the specimen was expected to slip only on the (111) [$\bar{1}$01] system. For room-temperature stress-strain experiments, deLamotte and Altstetter[2] found the critical resolved shear stress for slip on the fcc phase to be 1.26 ± 0.06 kg/mm^2.

The ends of the cylinder were polished flat and parallel to within ±200 μin. The crystal was then stressed until the first slip traces were observed. The stress was approximately 3 kg/mm^2, and the resolved shear stress was about 1.32 kg/mm^2. The crystal was again x-rayed and its slip traces were examined. Laue spots were found to be broadened. Slip traces over most of the crystal were of one orientation, indicating the dominance of a single slip system. The crystal was then cooled to 78 K.

Upon reexamining the crystal at room temperature, many additional traces were observed. These were indistinguishable from the slip traces, but were attributed to the phase transformation. About 60% of the specimen had transformation markings of one orientation. Laue spots from this section of the crystal were small and well defined, and they showed hexagonal symmetry. The crystal was reetched and no grain boundaries appeared. A cube was sparkmachined from the ingot with (1$\bar{2}$10), (10$\bar{1}$0), and (0001) faces. Herein, the plane normals to these faces are referred to as the *a*, *b*, and *c* axes, respectively; or as the 1, 2, and 3 axes when describing elastic constants. Laue back-reflection photographs showed the misorientations to be less than 1.0°. Opposite faces were polished flat and parallel to ±100 μin. The dimensions of the polished cube were about 10×10×10 mm, and the density was 8.8074 ± 0.006 g/cm^3.

B. Second-order elastic constants

For the fcc crystal five different measurements can be made to determine the three second-order elastic constants: C_{11} is determined from the propagation of longitudinal waves along [001]; C_{44} is determined from shear waves propagated along [110] (or [001]) and polarized along [001] (or [110]); the combination $C' = \frac{1}{2}(C_{11} - C_{12})$ is determined from shear waves propagated along [110] and polarized along [1$\bar{1}$0]; and the combination $C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ is determined from longitudinal waves propaged along [110].

For the hcp crystal only four of the five second-order elastic constants can be measured. The constants C_{11} and C_{33} are determined from the propagation of longitudinal waves in the basal plane and along the *c* axis, respectively. The constant $C_{66} = \frac{1}{2}(C_{11} - C_{12})$ is found from a shear wave propagated along the *a* (or *b*) axis and polarized along the *b* (or *a*) axis. The constant C_{44} is determined from the shear wave propagated along the *c* axis, and from the shear wave propagated along the *a* or *b* axis and polarized along the *c* axis. The constant C_{13} can only be determined from velocities of quasilongitudinal and quasishear waves propagating at some acute angle to the *c* axis. Following the procedure given by Fuller and Weston,[7] C_{13} can be estimated from the fcc elastic constants. The value of C_{13} used throughout this work is 0.954

TABLE I. Elastic constants of Co–32-wt.% Ni at 22 °C. Errors represent the consistency of the measurements. Entries are in units of 10^{12} dyn/cm^2.

Constant	Measured value
Cubic	
C_{11}	2.387 ± 0.008
C_{12}	1.553 ± 0.014
C_{44}	1.315 ± 0.006
Hexagonal	
C_{11}	3.260 ± 0.007
C_{12}	1.606 ± 0.010
C_{33}	3.584 ± 0.015
C_{44}	0.740 ± 0.010
C_{13}	...

$\times 10^{12}$ dyn/cm^2.

Second-order elastic constants were measured by a pulse-superposition method. Pulses were introduced into the sample by means of a 10-MHz quartz transducer bonded to the sample with phenyl salicylate (salol). An electronic system developed by Holder[8] was used.

The attenuation of all the modes in the fcc crystal is very large, as it is for pure nickel,[9] which is also fcc. This is due to ferromagnetic domain-boundary motion.[10] The attenuation can be significantly reduced by applying a transverse saturation magnetic field. The field necessary for saturation is about 5 kG. In pure cobalt, however, the attenuation problem is slightly modified. Below about 400 °C cobalt has the hcp structure, and at room temperature the attenuation of longitudinal modes is unaffected[11] by a magnetic field. However, shear-wave attenuation does depend on the magnetic field. For the hcp Co-Ni crystal, the attenuation of only the shear modes, especially C_{44}, is affected by the field. However, all measurements were made in a field of about 3.5 kG.

Results of the second-order elastic constant measurements for both crystals are listed in Table I. The absolute error for the hcp measurements is generally larger than for the fcc measurements because of the shorter transit times involved and because of higher attenuation. The fcc constants are within 2% of the extrapolated values of Leamy and Warlimont.[12]

C. Third-order elastic constants

The third-order elastic constants were determined by measuring the linear static-stress dependence of the velocities of small-amplitude sound waves. Both hydrostatic and uniaxial compression perpendicular to the wave propagation axis were used. All measurements were made in a saturation magnetic field. Hydrostatic pressure was applied by a nitrogen-gas tank and was measured with a Heise Bourdon gauge. The range of hydrostatic pressures used was 0–70 bars. The range of the uniaxial stress was 0–35 bars. For uniaxial stress measurements, the crystals were placed between shims to promote uniform compressional loading of the faces. Two types of shims were used: $\frac{1}{32}$-in. indium sheets and $\frac{1}{16}$-in. neoprene. A ball joint was placed between the rod and the upper plate to reduce the possibility of shearing the face of the specimen.

An important limitation in measuring small velocity changes arises from temperature drifts. A stress of 1 bar typically produces a relative velocity change of only several ppm. A 0.01 °C temperature change produces a similar velocity change. Thus, temperature control to within a few millidegrees is essential. The temperature was monitored with a Chromel advance thermocouple and could be determined to a millidegree. A heater coil around the sample raised its temperature several degrees above room temperature. A Honeywell temperature controller was used to regulate the heater current, with the amplified thermocouple signal serving as the feedback. The temperature could be controlled with this method to within several millidegrees.

For the fcc crystal 14 different measurements were made to determine the six third-order elastic constants. For the hcp crystal 16 different measurements were made to determine the ten third-order elastic constants. These measurements are listed in Tables II and III. For each measurement the directly measured quantity is the change in carrier frequency f with applied load P; this change was always found to be linear. A least-squares fit of the data was used to obtain $(1/f)\, \partial f/\partial P|_{T,P=0}$ for each measurement. This quantity is identi-

TABLE II. Sound-velocity stress experiments and results for cubic Co–32-wt.% Ni.

No.	Propagation axis	Polarization axis	Stress axis	$\frac{1}{W}\frac{\partial W}{\partial P}\Big\|_{T,P=0}$ (Mbar^{-1})
1	[001]	[001]	hydro	1.42 ± 0.04
2	[110]	[110]	hydro	1.45 ± 0.11
3	[001]	[110]	hydro	0.77 ± 0.03
4	[110]	[001]	hydro	0.99 ± 0.01
5	[110]	$[1\bar{1}0]$	hydro	0.82 ± 0.05
6	[001]	[001]	[110]	−0.24 ± 0.05
7	[110]	[110]	[001]	−1.21 ± 0.12
8	[110]	[110]	$[1\bar{1}0]$	0.39 ± 0.03
9	[001]	[110]	[110]	−0.71 ± 0.02
10	[001]	[110]	$[1\bar{1}0]$	−0.55 ± 0.01
11	[110]	[001]	[001]	1.13 ± 0.10
12	[110]	[001]	$[1\bar{1}0]$	−0.10 ± 0.04
13	[110]	$[1\bar{1}0]$	[001]	4.42 ± 0.02
14	[110]	$[1\bar{1}0]$	$[1\bar{1}0]$	−1.65 ± 0.07

TABLE III. Sound velocity stress experiments and results for hexagonal Co–32-wt.% Ni.

No.	Propagation axis	Polarization axis	Stress axis	$\frac{1}{W}\frac{\partial W}{\partial P}\Big\|_{T,P=0}$ (Mbar^{-1})
1	*a*	*a*	hydro	1.00 ± 0.13
	b	*b*	hydro	
2	*c*	*c*	hydro	1.27 ± 0.05
3	*a*	*b*	hydro	0.85 ± 0.13
	b	*a*	hydro	
4	*a*	*c*	hydro	0.77 ± 0.02
	b	*c*	hydro	
5	*c*	*a*	hydro	0.92 ± 0.06
	c	*b*	hydro	
6	*a*	*a*	*b*	-0.81 ± 0.05
7	*a*	*a*	*c*	-0.51 ± 0.19
	b	*b*	*c*	
8	*b*	*b*	*a*	-0.26 ± 0.05
9	*c*	*c*	*a*	-0.27 ± 0.14
	c	*c*	*b*	
10	*a*	*b*	*b*	1.60 ± 0.05
11	*a*	*b*	*c*	-1.03 ± 0.26
	b	*a*	*c*	
12	*b*	*a*	*a*	-2.05 ± 0.50
13	*a*	*c*	*b*	1.08 ± 0.28
	b	*c*	*a*	
14	*a*	*c*	*c*	1.69 ± 0.30
	b	*c*	*c*	
15	*c*	*a*	*a*	-1.96 ± 0.45
	c	*b*	*b*	
16	*c*	*a*	*b*	1.62 ± 0.23
	c	*b*	*a*	

cally equal to $(1/W)\,\partial W/\partial P|_{T,P=0}$, where $W = 2L_0/t$ is the natural sound velocity,[13] and L_0 is the unstressed path length. It is easily shown that

$$\frac{\partial}{\partial P}(\rho_0 W^2)\Big|_{T,P=0} = 2C\,\frac{1}{W}\frac{\partial W}{\partial P}\Big|_{T,P=0},$$

where $C = (\rho_0 W^2)_{T,P=0}$ is the appropriate second-order elastic constant. The relationships between the measured quantities $[\partial(\rho_0 W^2)/\partial P]_{T,P=0}$ and the second- and third-order elastic constants have been discussed by Thurston and Brugger.[14]

The stress coefficients of the natural velocity are summarized in Tables II and III. The errors indicate the range of the measured values.

From the hydrostatic-stress experiments, the pressure derivatives $\partial C/\partial P$ of the second-order elastic constants were calculated. It can easily be shown that

$$\frac{\partial C}{\partial P}\Big|_{T,P=0} = \frac{\partial}{\partial P}(\rho_0 W^2)\Big|_{T,P=0} + C(K - 2K_L),$$

where K is the isothermal bulk compressibility and K_L is the isothermal linear compressibility of the propagation axis (for cubic symmetry, $K_L = \frac{1}{3}K$). The values of the pressure derivatives for both the cubic and hexagonal phases are given in Table IV.

The hydrostatic and uniaxial data are then combined to obtain the third-order elastic constants. A least-squares program was used to determine the "best" values. For the fcc crystal, all the data are combined to determine the six constants. For the hcp crystal, the constants C_{133} and C_{333} are determined from measurements 2 and 9; the constants C_{111}, C_{112}, C_{113}, C_{123}, and C_{222} are determined from measurements 1, 3, and 6–12; the constants C_{144}, C_{155}, and C_{344} are determined from measurements 4, 5, and 13–16.

The complete sets of third-order elastic constants are presented in Table V. The errors indicate the standard deviations arising from the least-squares analysis and represent the consistency of the measurements.

As can be seen from Table V, the errors associated with the elastic constants of the hcp crystal are generally larger than those of the fcc crystal. Natural velocity changes could only be determined to a part in 10^6 for the hcp crystal, whereas a part in 10^7 was easily attainable for the fcc crystal. Two reasons can be given for this. First, the high attenuation in the hcp crystal results in fewer echoes in the echo train and thus less sensitivity with the pulse-superposition method. Second, the transit times for the hcp crystal are very short owing to its small size, and the present detection system was being pushed to the limits of its sensitivity. For example, the transit times for the longitudinal modes in this crystal are about 3 μsec, and the echoes themselves are normally of about 2 μsec duration. Thus, there is very

TABLE IV. Hydrostatic-pressure derivatives of second-order elastic constants of Co–32-wt.% Ni. Errors represent the range of several measurements.

C	$\left(\frac{\partial C}{\partial P}\right)_{T,P=0}$
Cubic	
C_{11}	7.35 ± 0.10
C_{44}	2.65 ± 0.20
C'	0.48 ± 0.20
Hexagonal	
C_{11}	7.08 ± 0.13
C_{33}	9.64 ± 0.05
C_{66}	1.57 ± 0.13
C_{44}	1.38 ± 0.07

TABLE V. Third-order elastic constants of Co–32-wt.% Ni at 22 °C. Entries are in units of 10^{12} dyn/cm^2.

Cubic	
$C_{111}=-25.48\pm0.73$	$C_{144}=-1.65\pm0.43$
$C_{112}=-12.12\pm0.42$	$C_{155}=-10.22\pm0.34$
$C_{123}=-0.14\pm0.77$	$C_{456}=-1.23\pm0.53$
Hexagonal	
$C_{111}=-46.68\pm2.30$	$C_{144}=-5.00\pm0.64$
$C_{112}=-5.64\pm1.54$	$C_{155}=1.78\pm0.78$
$C_{113}=1.86\pm1.34$	$C_{222}=-41.52\pm2.40$
$C_{123}=-2.56\pm2.88$	$C_{333}=-53.30\pm4.95$
$C_{133}=-3.37\pm2.06$	$C_{344}=-10.08\pm0.90$

little time between echoes, and separating the superimposed echoes from the pulses difficult. A solution to this problem is to decrease the pulse amplitude and pulse width, which results in a smaller echo train and less sensitivity.

III. DISCUSSION

In Sec. II, we have briefly discussed three observations that indicate that the transformed specimen is a hexagonal single crystal: Laue x-ray photographs show hexagonal-close-packed structure; surface markings indicate that the transformation occurred and that it was univariant; the magnetic field dependence of the attenuation of the longitudinal modes in the transformed specimen differs from that of the cubic specimen. The attenuation in the cubic specimen is similar to that found in nickel (fcc), and the attenuation in the transformed specimen is similar to that found in cobalt (hcp).

There is an additional indication that the transformed specimen is a hexagonal single crystal. This evidence arises from an analysis of the magnitude of the sound wave velocities and the symmetry of their polarizations.

As a result of the phase transformation, a [111] direction of the cubic system becomes the *c* axis of the hexagonal system. Also, a $[1\bar{1}0]$ direction corresponds to the *a* axis, and a $[11\bar{2}]$ direction corresponds to the *b* axis. It is possible to compare the symmetry of the elastic constants in a cubic system with [111], $[1\bar{1}0]$, and $[11\bar{2}]$ axes to that of the hexagonal system. It is easily shown[15] that the cubic elastic constants in this rotated coordinate system are

$$C_{11}^{*}=\tfrac{1}{6}(3C_{11}+3C_{12}+6C_{44}),$$

$$C_{33}^{*}=\tfrac{1}{6}(2C_{11}+4C_{12}+8C_{44}),$$

$$C_{12}^{*}=\tfrac{1}{6}(C_{11}+5C_{12}-2C_{44}),$$

$$C_{13}^{*}=\tfrac{1}{6}(2C_{11}+4C_{12}-4C_{44}),$$

$$C_{44}^{*}=\tfrac{1}{6}(2C_{11}-2C_{12}+2C_{44}),$$

$$C_{66}^{*}=\tfrac{1}{6}(C_{11}-C_{12}+4C_{44})=\tfrac{1}{2}(C_{11}^{*}-C_{12}^{*}),$$

$$C_{14}^{*}=\tfrac{1}{6}\sqrt{2}\,(C_{11}-C_{12}-2C_{44}),$$

where C_{ij}^{*} refers to the rotated coordinate system. In this system C_{33}^{*} can be determined from a longitudinal wave along the [111] direction, a pure-mode direction for cubic symmetry. Also, C_{11}^{*} can be determined from longitudinal waves along $[1\bar{1}0]$ or $[11\bar{2}]$. The $[1\bar{1}0]$ direction is a pure-mode direction for cubic symmetry; the $[11\bar{2}]$ direction is not. Similarly, the [111] direction is the only pure-shear-mode direction for a cubic crystal with these axes. In the hcp system, of course, all these modes are pure. Thus, an indication of crystal structure is provided by the pureness of the acoustic waves. If any of the modes are mixed modes, it indicates that the crystal is at least partially cubic rather than hexagonal. The best single indication using this method is perhaps the shear wave propagated along the *a* axis ($[1\bar{1}0]$ direction if cubic), and polarized along either the *c* axis ([111] direction) or the *b* axis ([112] direction). If the crystal is hexagonal, one measures either C_{44}^{hcp} or C_{66}^{hcp}. If the crystal is cubic, the shear wave will separate into both C_{44}^{fcc} and C'^{fcc} parts. These elastic constants, and thus the velocities, differ enough in magnitude to be easily identified.

All the acoustic waves propagated in the transformed crystal showed no evidence of cubic modes. In particular, the shear waves propagated along the *a* axis were pure modes, and the measured velocities (C_{44}^{hcp} velocity ≅ 2.9 mm/μsec, C_{66}^{hcp} velocity ≅ 3.1 mm/μsec) did not agree with the cubic velocities of either C_{44}^{fcc} (≅ 3.9 mm/μsec) or C'^{fcc} (≅ 2.2 mm/μsec).

The elastic-constant data are used, in the following section, to describe thermodynamic properties of the phase transition. It is of some interest, however, to consider the success or failure of the elastic constants in satisfying the Cauchy relations. These are simple relations that can be derived when atoms are at centers of symmetry and interact through central forces. For cubic symmetry the Cauchy relations are

$$C_{12}=C_{44},\quad C_{112}=C_{155},\quad C_{123}=C_{144}=C_{456}.$$

For hexagonal symmetry the Cauchy relations are

$$C_{13}=C_{44},\quad C_{12}=C_{66},$$

$$C_{166}=C_{112},\quad C_{344}=C_{133},\quad C_{155}=C_{113},$$

$$C_{266}=C_{122},\quad C_{456}=C_{366}=C_{144}=C_{123}.$$

Many of the hexagonal constants are not tabulated values, but linear combinations of them. The relations[16] and values are

$$C_{166}=\tfrac{1}{4}(3C_{222}-2C_{111}-C_{112})=-6.39,$$

$$C_{266}=\tfrac{1}{4}(2C_{111}-C_{222}-C_{112})=-11.55,$$

$$C_{366} = \tfrac{1}{2}(C_{113} - C_{123}) = 2.21 \, ,$$

$$C_{456} = \tfrac{1}{2}(C_{155} - C_{144}) = 3.39 \, ,$$

$$C_{122} = C_{111} - C_{222} + C_{112} = 10.80 \, ,$$

in units of 10^{12} dyn/cm^2.

For the cubic phase, for which each atom is at a center of symmetry, the Cauchy relations are nearly satisfied. This suggests that central-force-type interactions may be contributing dominantly to the elastic constants. If these forces are of short range, then the analysis given by Hiki and Granato[17] should apply here. They showed that for an fcc lattice with only nearest-neighbor central-force interactions the following relations should hold:

$$C_{11} = 2C_{12} = 2C_{44} \, ;$$

$$C_{111} = 2C_{112} = 2C_{155} \, ; \quad C_{123} = C_{456} = C_{144} = 0 \, .$$

To a first approximation, these relationships are somewhat satisfied for this alloy. It could be concluded that short-range repulsive forces, arising from d-shell overlap, contribute dominantly to higher-order elastic constants of fcc cobalt-nickel.

For the hexagonal phase the Cauchy relations are not as well satisfied. Since the interatomic forces would not be expected to change significantly because of the phase transition, the failure of the Cauchy relations is most likely due to the atoms of the hcp structure not being at centers of symmetry, thus resulting in internal-strain contributions to certain elastic constants.

IV. THERMODYNAMIC CALCULATIONS

The Gibbs free energy can be written

$$G = E - TS + PV - \sigma\epsilon \, , \tag{1}$$

where E, T, S, P, V, σ, and ϵ represent internal energy, absolute temperature, entropy, pressure, volume, shear stress, and shear strain, respectively. For two phases to coexist in equilibrium, the Gibbs free energies G of the two structures must be equal for a fixed temperature (T_0) and stress.

In general, however, there is an energy barrier opposing the transformation.[18] Physically, the energy barrier gives rise to a hysteresis loop surrounding the transformation temperature T_0. The transition temperature T_0 is normally taken as midway between the experimentally measured M_s and A_s temperatures.[4]

It is convenient to write the Gibbs free energy as

$$G = G_0 + G_t + PV - \sigma\epsilon \, , \tag{2}$$

where G_0 represents the stress-dependent static-lattice free energy and G_t represents the thermal energy of the system. To obtain G_0, a knowledge of the interatomic potential is required. However, G_t can be approximated using the Debye approximation.[19] G_t can then be written[20]

$$G_t = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \left[\tfrac{1}{2}\epsilon + \ln(1 - e^{-\epsilon})\right]\epsilon^2 \, d\epsilon \, , \tag{3}$$

where N is the number of particles, k_B is Boltzmann's constant, $\epsilon = h\nu/k_BT$, ν is the normal-vibration frequency, h is Planck's constant, $\Theta_D = h\nu_m/k_B$ is the Debye temperature, and ν_m is the cutoff normal-vibration frequency. The Debye temperature can be calculated from the sound velocities in the substance[20] and is proportional to a mean elastic-wave velocity:

$$\Theta = kv_m \, , \tag{4}$$

where

$$k = \frac{h}{k_B}\left(\frac{3}{4\pi V_a}\right)^{1/3} \, , \tag{5}$$

where V_a is the atomic volume. The velocity is given by the integration over all space:

$$3v_m^{-3} = \int \sum_{\alpha=1,2,3} v_\alpha^{-3} \frac{d\Omega}{4\pi} \, , \tag{6}$$

where v_1 is the quasilongitudinal wave velocity, v_2 and v_3 are the quasitransverse wave velocities, and $d\Omega$ is the increment of solid angle. Equation (6) can be numerically integrated using a computer. Phase velocities v_α are roots of the Christoffel equations

$$\det(C_{ijkl}\, x_j x_k - \rho v^2 \delta_{il}) = 0 \, , \tag{7}$$

which follow from equations of motion for plane, monochromatic waves,[21] where ρ is the mass density, C_{ijkl} is the fourth-rank elastic-constant tensor, x_j are components of the unit wave vector relative to cubic axes, and δ_{il} is the Kronecker δ. There are generally three distinct real roots of Eq. (7). The general secular equation and its solution is discussed in detail by Alers.[22]

It is of interest to consider the high-temperature limit of Eq. (3). For sufficiently high temperatures

$$G_t = 3Nk_BT \ln(\Theta_D/T) \tag{8}$$

and

$$S = 3Nk_B[1 - \ln(\Theta_D/T)] \, . \tag{9}$$

TABLE VI. Debye temperatures of Co–32-wt.% Ni, Co, and Ni.

	Elastic		Low-temp. specific heat	
Structure	fcc	hcp	fcc	hcp
Co-32-wt.% Ni	448.7 ± 2.5	468.3 ± 3.1	...	...
Nickel	476.2[a]	...	472.4 ± 1.4[b]	...
Cobalt	...	469.6[a]	...	460.3 ± 7.7[b]

[a] Reference 25. [b] Reference 26.

Then the difference in thermal energies between the two structures is

$$G_t^{(1)} - G_t^{(2)} = 3Nk_B T \ln(\Theta_1/\Theta_2) = T(S^{(2)} - S^{(1)}) , \tag{10}$$

where the superscripts and subscripts designate the two structures. Using Eq. (1) at the transition temperature T_0,

$$T_0 \Delta S = \Delta E + P\Delta V - \sigma \Delta\epsilon = \Delta H , \tag{11}$$

where the enthalpy H is given as $H = E + PV - \sigma\epsilon$. In Eq. (11) Δ represents quantities for structure 2 minus those for structure 1. Therefore, the enthalpy change upon transformation is

$$\Delta H = H^{(2)} - H^{(1)} = G_t^{(1)} - G_t^{(2)} = 3Nk_B T_0 \ln(\Theta_1/\Theta_2) = \Delta G_0 + P\Delta V - \sigma\Delta\epsilon . \tag{12}$$

The Debye temperatures for cubic and hexagonal Co–32-wt% Ni were calculated using the second-order elastic constants given in Table I. The Debye temperatures of Co–32-wt% Ni, are given in Table VI. The errors were estimated from the inaccuracy of the elastic constants. The Debye temperatures calculated for cobalt and nickel are also presented and compared with thermodynamic values determined from low-temperature specific-heat data. The agreement is satisfactory.

Rashid and Altstetter[6] reported the enthalpy change for the transformation in cobalt-nickel as approximately 100 cal/mole, although they suggest that as much as 15% of this could be due to defects. Using Eq. (12) with the calculated Debye temperatures for the two structures and taking the transition temperature as $T_0 = 323$ K ($A_s = 110\,^\circ$C, $M_s = -10\,^\circ$C) (Refs. 2 and 6) the calculated enthalpy change is about 82 cal/mole. If Eq. (3) is used to calculate the thermal energies, the result is $\Delta H = 90 \pm 15$ cal/mole, where the error has been estimated from the inaccuracies of the Debye temperatures. The reasonable accuracy of the simple high-temperature limit, Eq. (12) is expected since examination of the temperature dependence of the specific heat[23] in the Debye approximation shows the specific heat to be only 10% below the high-temperature limit when $T/\Theta_D \approx 0.6$.

The calculated free-energy change at zero stress and temperature (G_{00}) is given from Eq. (12) as 90 ± 15 cal/mole. As the only difference between the two structures is the different stacking requirement, we equate ΔG_{00} to the stacking-fault energy to obtain a stacking-fault energy of 12 ± 2 ergs/cm^2. This may be compared to a value determined by Ericcson,[24] by analysis of dislocation nodes in a Co–33-wt% Ni alloy. A temperature-dependent stacking-fault energy was found in this way. When Ericcson's result is extrapolated to $T = 0$, the stacking-fault energy is found to be about 20 ergs/cm^2. This is in reasonable agreement with the value calculated above.

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