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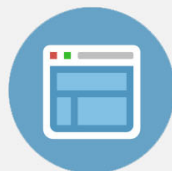
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Temperature dependence of the single-crystal elastic constants of Co-rich Co-Fe alloys*

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The single-crystal elastic moduli, C_{11} , C_{12} , and C_{44} of three fcc cobalt-iron alloys (Co-6 at.% Fe, Co-8 at.% Fe, Co-10 at.% Fe) were measured in the range 0–315 °C. In addition C_{11} for the Co-6 at.% Fe alloy, and $C' = (1/2)(C_{11} + C_{12} + 2C_{44})$ for the three alloys are measured over the temperature range 0–1250 °C. Plots of the elastic moduli vs temperature exhibit a change in slope and deviation from linearity in the neighborhood of the Curie temperature. The temperature variation of the shear anisotropy in the fcc phase $A_{fcc} (\equiv 2C_{44}/C_{11} - C_{12})$ differs among the three alloys. A_{fcc} exhibits a highly positive temperature dependence in the Co-10 at.% Fe alloy and a slight negative dependence in the Co-6 at.% Fe and Co-8 at.% Fe alloys. Previous statements in the literature that the hcp=fcc transformation in cobalt is preceded by a highly negative temperature dependence of the shear anisotropy ratio $A (\equiv C_{44}/C_{66})$ in the hcp phase between 523 °K and the transition at about 743 °K is not borne out by the present results. Rather it appears that the hcp=fcc transformation involves a change from $A > 1$ in the hcp phase to $A < 1$ in the fcc phase.

INTRODUCTION

Fisher and Dever¹ measured the single-crystal elastic constants C_{11} , C_{44} , C_{66} , C_{13} , and C_{12} in pure cobalt over the range 4–524 °K, and C_{33} over the range 4–711 °K. Based on these measurements and those of Fritz and Brugger (Ref. 1, private communication) on an fcc CO-8% Fe crystal at 300 °K, Fisher and Dever claimed that the hcp-fcc transformation in cobalt is preceded by highly negative temperature dependence of the shear anisotropy ratio $A (\equiv C_{44}/C_{66})$ in the hcp phase.

The present paper is concerned with the effects of temperature and % Fe on the single-crystal elastic constants of Co-rich cobalt-iron fcc solid solutions. Cobalt has an hcp structure, ϵ' phase, stable at temperatures below about 417 °C, and a fcc structure stable to its melting point (Fig. 1). Iron addition (at.% Fe $\leq 10\%$), however, stabilizes the fcc structure to well below 417 °C; it lowers considerably the temperature of the fcc=hcp transformation, Fig. 1. The boundary separating the hcp and fcc structures of the Co-rich Co-Fe solid solutions is not accurately known. Figure 1, for example, shows that at room temperature it is possible for the alloys with $6 \leq \text{at.}\% \text{ Fe} \leq 10$ to exist in the fcc structure. In fact, according to Hansen,² the two hcp=fcc transformation curves shown in Fig. 1 were obtained by averaging available data. A second point of interest to the present problem is the extent of the two-phase region, austenite + ferrite. Again the boundaries of this region are not accurately known. Figure 1 shows that at 300 °C the two-phase region extends from 25 to 10 at.% Fe. On the other hand, according to Lihl *et al.*,³ this zone, for alloys strongly contaminated with oxygen, extends from 26.5 to 7.5 at.% Fe. For the purpose of the present study, several Co- x at.% Fe single crystals, prepared from high-purity (0.9999) cobalt and iron, were obtained from Alpha Inorganic. The crystals were x-rayed at room temperature; only three crystals [Co-6 at.% Fe, Co-8 at.% Fe, and Co-10 at.% Fe] were found to be rather good single crystals with an fcc structure. Even then it is possible that the 10 at.% Fe crystal, and perhaps even the 8 at.% Fe crystal, contained minute traces of the ferrite phase which were not detected by the x-ray analysis. The samples were not analyzed for concentration gradients.

The present article reports on the temperature dependence of the elastic moduli C_{11} , C_{12} , and C_{44} of fcc Co-6 at.% Fe, Co-8 at.% Fe, and Co-10 at.% Fe alloys over the range 273–588 °K. In addition, C_{11} for the Co-6 at.% Fe alloy and $C' \equiv \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ for the three alloys were measured to temperatures above their Curie temperatures. The effect of the hcp=fcc transformation on the shear anisotropy ratio A is discussed.

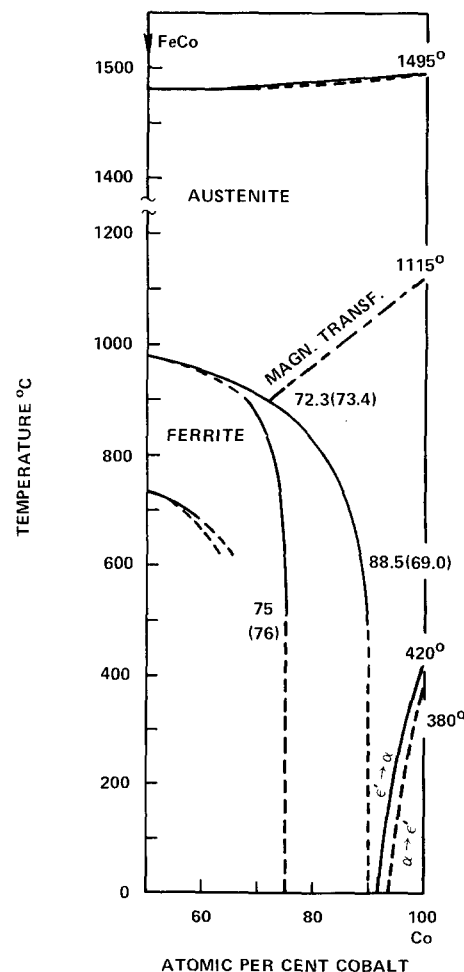


FIG. 1. The cobalt-rich part of the Co-Fe phase diagram. After Ref. 2.

TABLE I. Elastic moduli of an fcc Co-6 at. % Fe crystal as a function of temperature. C_{11}^* is calculated from propagating longitudinal waves in the [100] direction.

T (°C)	$C' \times 10^{-12}$ (dyn/cm ²)	$C'' \times 10^{-12}$ (dyn/cm ²)	$C_{44} \times 10^{-12}$ (dyn/cm ²)	$C_{11} \times 10^{-12}$ (dyn/cm ²)	$C_{11}^* \times 10^{-12}$ (dyn/cm ²)	$C_{12} \times 10^{-12}$ (dyn/cm ²)
0	3.08	0.37	1.26	2.19	...	1.45
25	3.07	0.37	1.24	2.20	2.18	1.46
33	3.02	0.37	1.23	2.16	2.17	1.42
46	3.02	0.37	1.22	2.17	2.16	1.43
63	2.98	0.36	1.21	2.13	2.14	1.41
76	2.98	0.36	1.21	2.13	2.13	1.41
88	2.94	0.36	1.20	2.10	2.12	1.38
98	2.97	0.36	1.19	2.14	...	1.42
108	2.96	0.36	1.18	2.14	2.11	1.42
118	2.89	0.36	1.18	2.07	2.10	1.35
132	2.89	0.36	1.17	2.08	...	1.36
150	2.82	0.35	1.16	2.01	2.07	1.31
168	2.84	0.35	1.17	2.02	2.04	1.32
187	2.85	0.35	1.17	2.03	2.03	1.33
202	2.81	0.35	1.14	2.02	2.02	1.32
215	2.81	0.35	1.14	2.02	2.00	1.32
230	2.76	...	1.13	...	1.99	...
250	2.73	0.35	1.12	1.96	1.98	1.26
270	2.71	0.34	1.11	1.94	1.98	1.26
300	2.69	0.34	1.10	1.93	1.93	1.25
315	2.68	0.34	1.10	1.92	1.92	1.24

EXPERIMENTAL PROCEDURE

The cylindrical single crystals of Co- $x\%$ Fe obtained from Alpha Inorganic, were cut, with a Metals Research Ltd. servomet spark cutter, into right circular cylindrical samples with end faces perpendicular to [110] and [100] directions. These single crystals were then hand lapped until the faces were flat and parallel to within ± 0.004 cm.

The wave velocities were determined by a pulsed ultrasonic method⁴ using a Matec 900 model ultrasonic Attenuation Comparator. One-half-in. -diam x -cut or ac -cut quartz transducer of 15 MH and overtone polish were used. Quartz undergoes a phase transformation at 511 °C. Therefore, in order to maintain the transducer below this transformation temperature, measurements were made using the buffer-rod technique.⁵ This technique is not very suitable for measuring transverse waves. Therefore, only longitudinal waves were propagated to temperatures above the Curie temperatures of the alloys. A fused silica buffer rod 1.84 cm in diameter and 20 cm in length was used. The end of the rod, where the transducer was attached, was maintained at temperatures below the phase transformation of quartz. The temperature measurements were made using chromel-alumel thermocouples attached to the specimen.

The coupling cement for attaching the sample and the transducer to the buffer rod for longitudinal wave propagation, and for attaching the transducer to the sample for shear wave propagation, was a quasiwater glass cement.⁶ It consists of 5 parts by weight of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) and 1 part by weight of calcium carbonate with a liquid solution of sodium silicate (density 40° Baume). The ratio used was 1.5 g power/80 mliter liquid mixture. The cement was allowed to set for 72 h prior to placing the sample in the furnace. Measurements of the elastic constant were

carried out in an argon atmosphere. Several runs were necessary to measure the longitudinal wave velocity, due to interruptions by the breakage of the acoustic coupling cement. The best heating rate was found to be 1 °C/min in the temperature range 0–500 °C and 3 °C/min in the range 500–1250 °C; wave velocity measurements for temperatures above 1250 °C were not possible because of the deterioration of the acoustic bond. Measurements of ultrasonic velocities to temperatures as high as 3000 °C, using mechanical coupling, have been reported in the literature.⁵ However, this was not possible in the present experiment due to the small size of the samples available to us, and because the single crystals could not be subjected to high stresses for the fear of recrystallization. The shear wave veloci-

TABLE II. Elastic moduli of an fcc Co-8 at. % Fe crystal as a function of temperature.

T (°C)	$C' \times 10^{-12}$ (dyn/cm ²)	$C'' \times 10^{-12}$ (dyn/cm ²)	$C_{44} \times 10^{-12}$ (dyn/cm ²)	$C_{11} \times 10^{-12}$ (dyn/cm ²)	$C_{12} \times 10^{-12}$ (dyn/cm ²)
0	2.89	0.29	1.19	1.99	1.41
25	2.87	0.29	1.18	1.98	1.40
33	2.86	0.29	1.18	1.97	1.39
46	2.85	0.29	1.16	1.98	1.40
63	2.84	0.29	1.16	1.97	1.39
76	2.82	0.28	1.14	1.96	1.39
88	2.82	0.28	1.15	1.95	1.39
98	2.83	0.28	1.15	1.95	1.39
108	2.80	0.28	1.14	1.94	1.38
118	2.76	0.28	1.13	1.91	1.35
132	2.74	0.28	1.13	1.89	1.33
150	2.72	0.28	1.12	1.88	1.32
168	2.72	0.28	1.12	1.88	1.32
187	2.68	0.28	1.11	1.85	1.29
202	2.68	0.28	1.10	1.86	1.30
215	2.65	0.27	1.10	1.83	1.28
230	2.64	0.27	1.09	1.83	1.28
250	2.68	0.27	1.09	1.80	1.32
270	2.61	0.27	1.08	1.80	1.26
300	2.59	0.27	1.07	1.79	1.25
315	2.59	0.27	1.06	1.80	1.26

TABLE III. Elastic moduli of an fcc Co-10 at. % Fe crystal as a function of temperature.

T (°C)	$C' \times 10^{-12}$ (dyn/cm ²)	$C'' \times 10^{-12}$ (dyn/cm ²)	$C_{44} \times 10^{-12}$ (dyn/cm ²)	$C_{11} \times 10^{-12}$ (dyn/cm ²)	$C_{12} \times 10^{-12}$ (dyn/cm ²)
0	2.61	0.22	1.08	1.77	1.30
25	2.59	0.22	1.08	1.73	1.29
33	2.59	0.21	1.07	1.73	1.29
46	2.53	0.21	1.07	1.67	1.25
63	2.50	0.21	1.06	1.65	1.23
76	2.51	0.21	1.05	1.67	1.25
88	2.51	0.21	1.05	1.67	1.25
98	2.47	0.21	1.05	1.63	1.21
108	2.47	0.20	1.04	1.63	1.23
118	2.44	0.20	1.04	1.61	1.19
132	2.46	0.20	1.03	1.63	1.23
150	2.44	0.20	1.03	1.61	1.21
168	2.43	0.20	1.03	1.61	1.20
187	2.41	0.19	1.02	1.58	1.20
202	2.41	0.19	1.01	1.58	1.20
215	2.37	0.19	1.01	1.56	1.16
230	2.38	0.19	1.00	1.57	1.16
250	2.35	0.18	1.00	1.53	1.15
270	2.35	0.18	0.99	1.54	1.18
300	2.30	0.18	0.99	1.49	1.13
315	2.30	0.18	0.98	1.50	1.14

ty measurements were not possible for temperatures above 315 °C because of very strong attenuation; several kinds of cement were tried without success. Similar difficulties were reported by Fisher and Dever in measuring the elastic constants of pure hcp cobalt.

The fcc cobalt-iron alloys have three independent elastic constants: C_{11} , C_{12} , and C_{44} . From measurements of the elastic wave velocities, longitudinal and shear, in a [110]-oriented crystal, we obtained directly three independent linear combinations of these elastic constants,

$$C_{44}, \quad C'' = \frac{1}{2}(C_{11} - C_{12}), \quad C' = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}). \quad (1)$$

These measurements were used to calculate C_{44} , C_{11} , and C_{12} . One cylindrical sample of the Co-6 at. % Fe alloy was prepared with the parallel faces normal to the [100] direction. A determination of the longitudinal wave velocities in this sample allowed a direct computation of C_{11} . These independent measurements, compared with the values of C_{11} calculated from Eq. (1), provided a check of reproducibility.

Sources of error

Several sources of scatter error are inherent in the technique employed. Although the end faces of each

sample and buffer rod were precisely machined for smooth contact with the transducer, any unevenness of these surfaces would result in an error in the observed values of the wave velocities, and hence, in the corresponding values of the dynamic moduli. Also the instability of the cement to the propagation of ultrasonic waves is believed to be the cause of the scatter observed in the plots of the dynamic moduli vs temperature at the lower temperatures. An average error of 0.05% was found in the time measurements. An over-all error of 1% is assigned to the values of C_{44} , C' , and C'' . The accuracy of the derived constants C_{11} and C_{12} is less, of course, due to error propagation.

Temperature corrections

Very small temperature corrections of the measured elastic constants were necessary. For example, the longitudinal velocity V_L is

$$V_L = [(1/2\rho)(C_{11} + C_{12} + 2C_{44})]^{1/2} \equiv (C/\rho)^{1/2} = 2d/t, \quad (2)$$

where d is the length of the sample and t is the time. Above room temperature

$$d^2 \approx d_0^2(1 + 2\alpha\Delta T), \quad (3)$$

$$\rho = \rho_0(1 + 3\alpha\Delta T)^{-1} \quad (4)$$

or

$$C_T = C_0 \frac{1 + 2\alpha\Delta T}{1 + 3\alpha\Delta T} \approx C_0(1 - \alpha\Delta T), \quad (5)$$

where ρ_0 , d_0 , and C_0 are the density, length, and elastic modulus at room temperature, respectively, and α is the thermal expansion coefficient. Using the value of α for pure cobalt,⁷ $\alpha = 1.8 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, in Eq. (5), the temperature corrections become negligible.

RESULTS AND DISCUSSION

Values of C' , C'' , C_{44} , C_{11} , and C_{12} for the three alloys, in the range 273–588 °K are given in Table I–III. These results show that the elastic moduli decrease linearly with increasing temperature. The variation of the moduli with % Fe is determined as follows. Fisher and Dever derived the following relations among the moduli of the fcc and the hcp phases:

$$C_{33} : \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44}) \equiv C'_{33}, \quad (6a)$$

$$C_{11} : \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) \equiv C'_{11}, \quad (6b)$$

$$C_{13} : \frac{1}{3}(C_{11} + 2C_{12} - 2C_{44}) \equiv C'_{13}, \quad (6c)$$

TABLE IV. Computed room-temperature values of elastic moduli in fcc Co-Fe alloys corresponding to the elastic moduli in the hcp phase of cobalt [see Eq. (6)]. The prime indicates values computed as per Eq. (6).

	$C_{33} \times 10^{-12}$ (dyn/cm ²)	$C_{11} \times 10^{-12}$ (dyn/cm ²)	$C_{13} \times 10^{-12}$ (dyn/cm ²)	$C_{44} \times 10^{-12}$ (dyn/cm ²)	$C_{66} \times 10^{-12}$ (dyn/cm ²)	$A = C_{44}/C_{66}$
Co	3.574 ^a	3.063 ^a	1.019 ^a	0.753 ^a	0.706 ^a	1.06 ^a
	$C'_{33} \times 10^{-12}$ (dyn/cm ²)	$C'_{11} \times 10^{-12}$ (dyn/cm ²)	$C'_{13} \times 10^{-12}$ (dyn/cm ²)	$C'_{44} \times 10^{-12}$ (dyn/cm ²)	$C'_{66} \times 10^{-12}$ (dyn/cm ²)	$A' = C'_{44}/C'_{66}$
Co-6 at. % Fe	3.36	3.07	0.88	0.66	1.9	0.35
Co-8 at. % Fe	3.166 3.524 ^b	2.87 3.229 ^b	0.807 1.022 ^b	0.587 0.66 ^b	1.766 0.956 ^b	0.33 0.69 ^b
Co-10 at. % Fe	2.88	2.59	0.716	0.507	1.586	0.32

^aReference 1.

^bAfter Fritz and Brugger (Ref. 1).

TABLE V. Values of C_{14} (rhombohedral) computed from Eq. (7) and measured values of C_{11} , C_{12} , and C_{44} .

Alloy	T (°C)	C_{14} (rhombohedral) $\times 10^{-12}$ (dyn/cm ²)
Co-6 at. % Fe	0	-0.418
	315	-0.357
Co-8 at. % Fe	0	-0.423
	315	(-1.090) ^a -0.370
Co-10 at. % Fe	0	-0.397
	315	-0.376

^aRoom-temperature value of Fritz and Brugger (Ref. 1).

$$C_{44}: \quad \frac{1}{3}(C_{11} - C_{12} + C_{44}) \equiv C'_{44}, \quad (6d)$$

$$C_{66}: \quad \frac{1}{3}(C_{11} - C_{12} + 4C_{44}) \equiv C'_{66}. \quad (6e)$$

In true hexagonal symmetry C_{14} is equal to zero and therefore is omitted from Eqs. (6a)–(6e). Smith suggested however, that an fcc crystal when indexed on hexagonal axes is actually in a lower point group and is rhombohedral. Therefore, C_{14} need not be identically zero but is

$$C_{14}(\text{rhombohedral}) = \sqrt{2}/6(C_{11} - C_{12} - 2C_{44})(\text{cubic}) \equiv C'_{14}. \quad (7)$$

Equations (6a)–(6e) were used to calculate C'_{33} , C'_{11} , C'_{13} , C'_{44} , C'_{66} , and the corresponding shear anisotropy ratio of the hcp phase A' ($\equiv C'_{44}/C'_{66}$) for the present alloys. The computed room-temperature results, and the measurements of Fisher and Dever for hcp cobalt are given in Table IV. The results of Fritz and Brugger for an fcc Co-8 % Fe crystal at 300 °K are also included in Table IV. The results of Fritz and Brugger differ substantially, in magnitude, from the present results. We cannot offer any discussion of this difference because details of the measurements and the results, e.g., C_{11} , C_{12} , etc., of these authors were not published; only the computed values C'_{33} , etc., were merely quoted by Fisher and Dever as a private communication.

The results in Table IV show that¹ the moduli C'_{33} , C'_{11} , etc., decrease with increasing at. % Fe.² The present calculated moduli C'_{33} , etc. (with exceptions for C'_{66}), are close in value to the measurements of Ref. 1 for pure hcp cobalt.³ The constants C'_{33} , etc., exhibit the same trend as do the constants C_{33} , etc., namely, $C'_{33} > C'_{11} > C'_{13} > C'_{44}$.⁴ The results of Fritz and Brugger for the Co-8% Fe alloy are much closer to the pure cobalt results than to our present results for the Co-8 at. % Fe alloy.⁵ In reference to the shear constant C'_{66} , both the present results and the results of Fritz and Brugger, although different in magnitude, exhibit the same trend; namely, $C'_{66} > C'_{44}$.

Fisher and Dever suggested that the large differences between the measured values of the shear moduli C_{44} , C_{66} , and the shear anisotropy ratio A , and the corresponding computed values A' , C'_{44} , and C'_{66} , indicate that the hcp \rightleftharpoons fcc transformation involves¹ either an abrupt change from $A > 1$ in the hcp phase to $A < 1$ in the fcc phase, or² a large negative temperature dependence of A in the hcp phase between 523 °K and

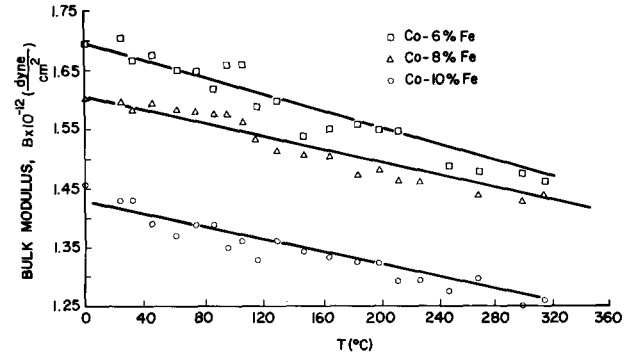


FIG. 2. Variation of the bulk modulus B with temperature.

the transition at about 743 °K. The present results between 523 and 588 °K do not support the latter possibility. Rather, the fact that the results for pure hcp cobalt¹ show $A > 1$, and the present results and those of Fritz and Brugger show that $A < 1$ in the fcc cobalt-iron alloys (see Table IV), support the former possibility.

Values of C_{14} (rhombohedral) computed from Eq. (7), and data in Tables I–III, were different from zero and negative. Computer C_{14} (rhombohedral) values at 0 and 315 °C for the present alloys, and the room-temperature value of Fritz and Brugger are given in Table V. It is seen that the present values are closer to zero than the value of Fritz and Brugger. It is also noted that as the temperature increases, the value of C_{14} (rhombohedral) approaches zero more closely, and the values for the Co-10 at. % Fe alloy are closer to zero than are the values of the Co-6 at. % Fe alloy. This behavior is to be expected from an examination of Fig. 1. The nonzero values of C_{14} (rhombohedral) may have resulted, as suggested by Smith, from the hcp \rightleftharpoons fcc transformation taking place during the measurements in the 0–315 °C temperature range. This transformation, however, could have taken place only to a very limited extent, because our x-ray analysis, at room temperature, showed the crystals to be of fcc structure; needle-like zones of the hcp or the rhombohedral phase may have formed upon cooling to 0 °C, and were redissolved, however, partially or completely, upon reheating. In any event, the present measurements do not allow more

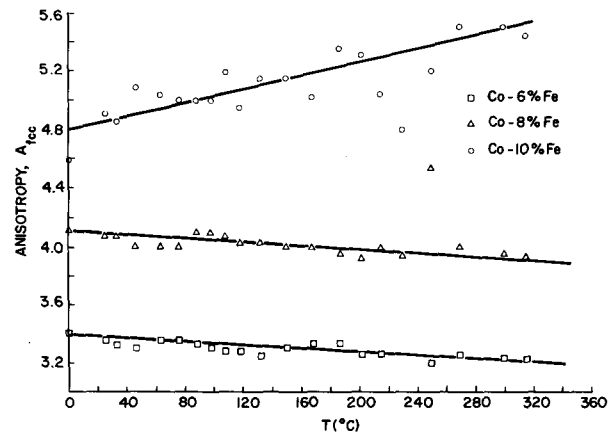


FIG. 3. Variation of the fcc anisotropy ratio A_{fcc} with temperature.

TABLE VI. Elastic moduli of Co-Fe crystals as a function of temperature.

T (°C)	Co-6 at. % Fe	Co-6 at. % Fe	Co-8 at. % Fe	Co-10 at. % Fe
	$C_{11} \times 10^{-12}$ (dyn/cm ²)	$C' \times 10^{-12}$ (dyn/cm ²)	$C' \times 10^{-12}$ (dyn/cm ²)	$C' \times 10^{-12}$ (dyn/cm ²)
330	...	2.64	2.56	...
350	...	2.64	2.52	2.28
370	...	2.64	2.56	2.28
390	...	2.53	2.52	2.27
430	1.84	2.50	2.48	2.22
450	1.82	2.47	2.44	2.19
470	1.82	2.44	2.44	2.19
498	1.80	2.42	2.43	2.19
521	1.76	2.42	2.38	2.11
577	1.72	2.33	2.35	2.06
605	1.71	2.26	2.34	2.00
630	1.66	2.24	2.30	2.00
698	1.64	2.16	2.26	1.96
715	1.63	2.14	2.21	1.90
745	1.63	2.10	2.20	1.90
779	1.56	2.06	2.18	1.89
791	1.54	2.04	2.16	1.88
814	1.52	2.02	2.15	1.84
845	1.51	1.98	2.14	1.81
867	1.51	1.96	2.10	1.79
881	1.49	1.94	2.07	1.73
898	1.49	1.92	2.07	1.73
908	1.43	1.91	2.05	1.73
941	1.40	1.88	2.05	1.73
962	1.37	1.86	2.04	1.69
984	1.35	1.86	2.02	1.65
1001	1.31	1.80	1.99	1.65
1025	1.31	1.76	1.99	1.61
1047	1.29	1.72	1.98	1.60
1078	1.27	1.68	1.98	1.56
1082	1.27	1.68	1.97	1.53
1091	1.27	1.66	1.97	1.53
1100	1.26	1.60	1.97	1.49
1115	1.26	1.59	1.97	1.49
1121	1.25	1.57	1.96	1.49
1149	...	1.55	1.95	1.45
1168	...	1.54	1.93	1.42
1198	...	1.53	1.92	1.40
1210	...	1.51	1.91	1.39
1250	...	1.49	...	1.38

definitive conclusions regarding the hcp=fcc transformation.

The present results allow the computation of the bulk modulus B from

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (8)$$

and the anisotropy in the fcc phase A_{fcc} from

$$A_{fcc} = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (9)$$

The variation of B and A_{fcc} with temperature, for each of the alloys, is shown in Figs. 2 and 3, respectively. B is found to decrease with increasing % Fe and decrease linearly with temperature in the range 0–315 °C. The rate of decrease of B with temperature is about the same in the three alloys. On the other hand, A_{fcc} has a small negative temperature dependence in the Co-6 at. % Fe and Co-8 at. % Fe alloys and a strong positive temperature dependence in the Co-10 at. % Fe alloy. This qualitative difference in the temperature dependence of A_{fcc} between the Co-10 at. % Fe alloy and the other two alloys may be related to the formation of the two-phase

structure (austenite + ferrite) at about 10 at. % Fe; it is possible that some minute amounts of the ferrite phase precipitated out upon cycling the Co-10 at. % Fe crystal in the range 0–315 °C.

Values of C' , for the three alloys, in the temperature range 330–1250 °C are given in Table VI and plotted in Fig. 4. Values of C_{11} for the Co-6 at. % Fe alloy in the range 330–1250 °C are also given in Table VI, and plotted in Fig. 4. It must be stated that the slopes in the paramagnetic region are not well established. Only few measurements could be made at $T > 1200$ °C because of difficulties associated with the stability of the acoustic bonding material. Figure 4 shows that the elastic moduli vary fairly linearly with temperature, except for a region around the Curie temperature. This behavior is true for most ferromagnetic materials.⁸

The elastic constants of a crystal are calculated by obtaining the second derivative of the total energy E of the crystal with respect to strain

$$C_{ij} = \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j}, \quad (10)$$

where i and j are the directions of propagation and displacement of an acoustic wave, respectively. For a ferromagnetic crystal the total Hamiltonian H can be written

$$H = H_{ex} + H_{ct} + H_{ms}, \quad (11)$$

where these terms represent the exchange, crystal field, and magnetostrictive contributions, respectively. The magnetostrictive term can be written⁹

$$H_{ms} = H_E + H_M, \quad (12)$$

where H_E is the contribution to the elastic energy due to homogeneous strain components, and H_M is due to the magnetoelastic interaction. Therefore, elastic constants are sensitive, as seen in Fig. 4, to changes in magnetic structure, because of changes in the magnetostrictive term in the Hamiltonian. The elastic constants in the ferromagnetic and paramagnetic phases are very important basic physical constants, because they are related to the first and second derivatives of the exchange energy $J(r)$ with respect to the interatomic distance. Measurements of volume magnetostriction and thermal expansion give only the first derivative of the exchange energy. In the Ising model i. e., the localized model of ferromagnetism, the energy E of a ferromagnetic crystal can be written approximately as⁸

$$E = E_0 - \frac{1}{2} N z (M/M_0)^2 J(r), \quad (13)$$

where M/M_0 is the relative magnetization, z is the number of nearest neighbors, N is the number of atoms per unit volume, and E_0 is the sum of all energies not related to the alignment of magnetic moments. It follows from this relation that for an fcc metal, the adiabatic (at fixed magnetization) elastic constants at the equilibrium distance r_0 are⁸

$$C' = C^0 - \frac{N}{4} \left(\frac{M}{M_0} \right)^2 \left(\frac{r_0^2}{3} \frac{d^2 J}{dr^2} + 13 r_0 \frac{dJ}{dr} \right), \quad (14)$$

$$C_{44} = C_{44}^0 - \frac{N}{4} \left(\frac{M}{M_0} \right)^2 \left(r_0^2 \frac{d^2 J}{dr^2} + 7 r_0 \frac{dJ}{dr} \right), \quad (15)$$

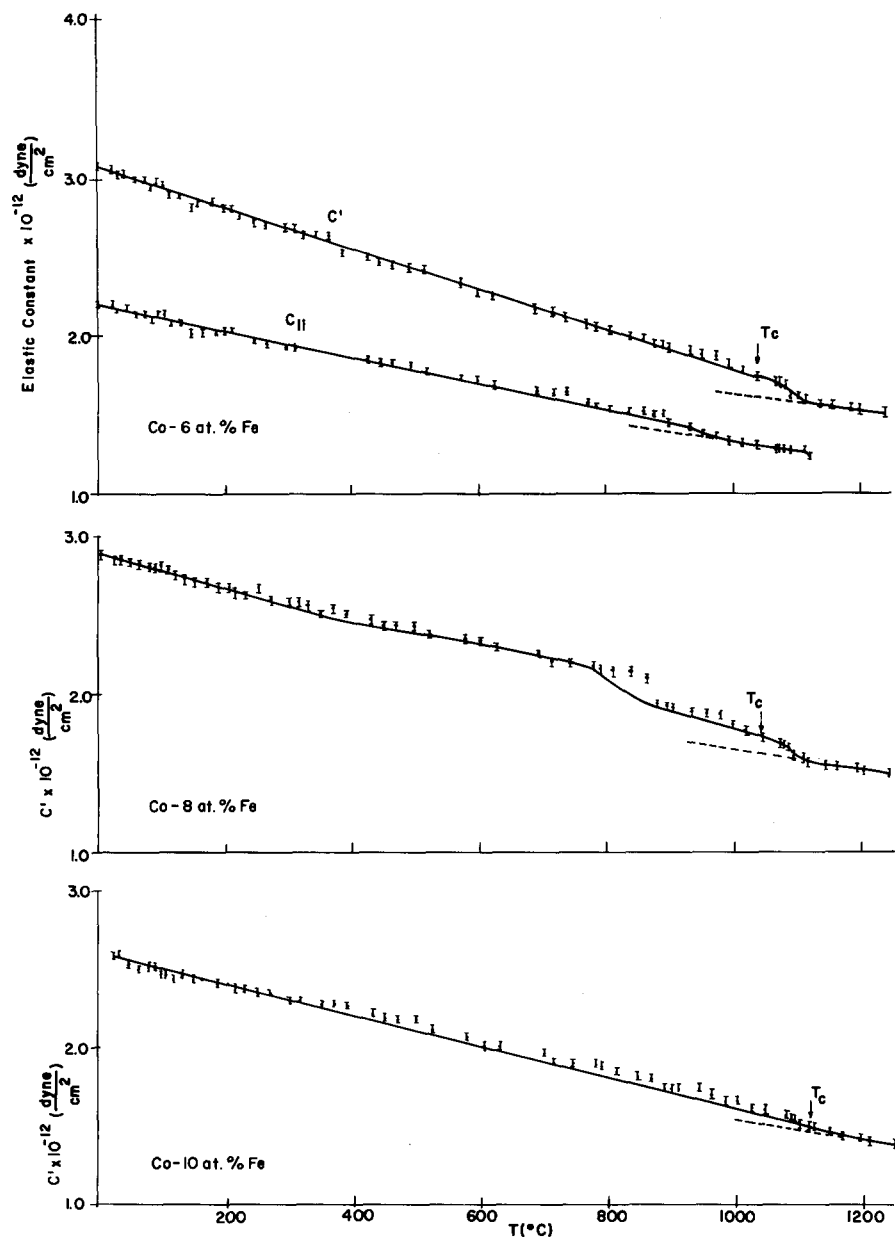


FIG. 4. Variation of the elastic moduli C_{11} and C' with temperature.

$$B = \frac{1}{3}(C_{11} + 2C_{12})$$

$$= B^0 - \frac{2N}{3} \left(\frac{M}{M_0} \right)^2 \gamma_0^2 \frac{d^2 J}{dr^2}, \quad (16)$$

where $C^{0'}$, C_{44}^0 , and B^0 represent values of the elastic constants C' , and C_{44} and the bulk modulus B in the absence of a ferromagnetic phase change (that is, these would be the low-temperature values obtained by extrapolation from the high-temperature paramagnetic data). If the relative magnetization is known, extrapolated values of the elastic constants from the paramagnetic region on the ferromagnetic region can be used to calculate dJ/dr and $d^2 J/dr^2$ from Eqs. (14)–(16).

The explanation for the departure from linearity when a material is cooled through the Curie temperature can be given here only on a qualitative basis. A quantitative calculation would require (i) a detailed knowledge of the band structure of the metal, and (ii) that a collective

model, rather than the Ising model, of ferromagnetism be used. A very simple phenomenological explanation of this behavior is that changes in volume magnetostriction that occur around the Curie temperature cause changes in the derivatives of the elastic energy with respect to strain and a subsequent change in the elastic constants; Bozorth¹⁰ gives, e.g., the relations between volume magnetostriction and the elastic constants for cubic crystals. In other words, as a ferromagnetic substance is cooled through the Curie temperature, changes in the relative alignment of the magnetic moments give rise to a change in those contributions to the total energy of the crystal which arise from interatomic magnetic interactions. Since the elastic constants are derivatives of this total energy with respect to strain, an intrinsic magnetic contribution to the elastic constants should appear.

Döring¹¹ proposed an explanation of the magnetic effect by means of a relaxation mechanism based on changes in the spontaneous magnetization accompanying the

changes in volume which occur during the measurements of the moduli. Since the spontaneous magnetization depends primarily on volume, the modulus C' , which is measured from a longitudinal wave distortion, should be more affected by the magnetic transformation than is C_{44} or C'' . One should note however that not only the magnitude of the spontaneous magnetization but also its directional changes are due to the deformations which are produced when measuring the elastic constants. In the present experiment we were unable to measure the shear moduli C_{44} or C'' in the paramagnetic phase. However, for the Co-6 at. % Fe crystal both C_{11} and C' were measured to temperatures above the Curie temperature. These results (Fig. 4) show that C' is more affected by the magnetic transformation than is C_{11} .

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