

Low-temperature manganese contributions to the elastic constants of face-centred-cubic Fe–Cr–Ni stainless steel

H. M. LEDBETTER, S. A. KIM

Fracture and Deformation Division, Institute for Materials Science and Engineering, National Bureau of Standards, Boulder, Colorado 80303, USA

By ultrasonic methods, we determined the elastic constants between 295 and 4 K of nominally Fe–18Cr–8Ni alloys (in wt%) containing up to 6% manganese. We report five elastic constants: C_1 = longitudinal modulus, B = bulk modulus, E = Young modulus, G = shear modulus, and ν = Poisson ratio. At all temperatures, manganese lowers all these elastic constants. With the exception of ν , larger reductions occur at 4 K than at 295 K. At 4 K, the bulk modulus decreases more than the shear modulus: approximately 0.54 and 0.30% per per cent manganese, respectively. Manganese raises the magnetic-transition temperature, which occurs between 40 and 90 K, by approximately 9 K per per cent manganese. A simple model predicts the volume increase accompanying Mn alloying. However, a simple model fails to predict the elastic-constant reductions; this suggests magnetic interatomic interactions.

1. Introduction

We reported previously [1] the ambient-temperature contribution of manganese to the elastic constants of face-centred-cubic (fcc) Fe–Cr–Ni alloys. Nominally, these alloys contained 18% chromium and 8% nickel (mass percentage). Our results showed that manganese lowers all the elastic-stiffness constants and the Poisson ratio. The largest effect occurred in the bulk modulus:

$$\frac{\Delta B}{cB} = -0.47 \quad (1)$$

Here c denotes fractional manganese concentration. Thus, the bulk modulus decreases approximately 0.5% per per cent solute. As the atomic mass of manganese (54.94) differs only slightly from the alloy's effective atomic mass (55.33), differences between atomic and mass percentages are small. Here, for the same polycrystalline alloys, we report further studies: elastic-constant measurements between 295 and 4 K. These studies answer two questions. First, how does the low-temperature magnetic phase transition affect the elastic constants? Second, does the manganese-concentration dependence at 4 K resemble that at 295 K? In studying similar Fe–Cr–Ni alloys alloyed with interstitial carbon and nitrogen, Ledbetter *et al.* [2] found strongly different composition effects at 4 and 295 K.

Previously [1], we described the peculiar atomic properties of manganese and their possible effect on alloy physical properties. These peculiarities include a 58-atom unit cell, a bulk modulus 0.35 times that of iron (despite similar atomic volumes), antiferromagnetic electronic interactions, and negative low-temperature thermal expansivity.

We determined the elastic constants by measuring mass density and the near-10 MHz ultrasonic velocities.

2. Measurements

Most of the measurement details have been reported previously [1]. We achieved low-temperature measurements to 4 K using procedures described by Naimon *et al.* [3].

3. Results

For both 295 and 4 K, Table I shows for 10 alloys the following measured and computed quantities; ρ the mass density, v_l the longitudinal sound velocity; v_t the transverse sound velocity; C_1 the longitudinal modulus = ρv_l^2 ; G the shear modulus = ρv_t^2 ; B the bulk modulus = $C_1 - 4G/3$; E the Young modulus = $9GB/(3B + G)$; and ν the Poisson ratio = $[E/(2G)] - 1$. For 295 and 4 K, Figs 1 and 2 show graphs of the measured quantities plotted against composition.

For one alloy, Fig. 3 shows the temperature variation of the elastic constants.

Fig. 4 shows the effect of Mn on the magnetic-transition temperature. We estimated that the transition temperature for both v_l and v_t corresponds to the temperature halfway between the maximum and minimum sound velocities. Also in Fig. 4, we include results from magnetic-susceptibility measurements [4].

4. Discussion

First, we consider volume effects. Uncorrected for chromium and nickel fluctuations, our mass-density measurements give the volume change

$$\frac{\Delta V}{cV} = -\frac{\Delta \rho}{\rho} = 0.092 \quad (2)$$

Here, c denotes fractional manganese concentration. Thus, one percent of Mn raises the effective atomic volume approximately 0.1%. Many models exist for

TABLE I Measured and derived quantities

Mn (mass %)	ρ (g cm ⁻³)	v_1 (cm μ sec ⁻¹)	v_1 (cm μ sec ⁻¹)	C_1 (GPa)	G (GPa)	B (GPa)	E (GPa)	ν
<i>T</i> = 295 K								
1.02	7.904	0.5752	0.3145	261.5	77.18	157.3	201.2	0.287
2.01	7.861	0.5761	0.3145	260.9	77.75	157.2	200.3	0.288
3.85	7.875	0.5738	0.3143	259.3	77.79	155.6	200.0	0.286
5.81	7.862	0.5717	1.3131	257.0	77.08	154.2	198.2	0.286
<i>T</i> = 4 K								
1.02	7.975	0.5783	0.3206	266.7	81.94	157.4	209.5	0.278
2.01	7.931	0.5794	0.3204	266.2	81.39	157.7	208.3	0.280
3.85	7.9448	0.5761	0.3193	263.7	80.98	155.7	207.0	0.278
5.81	7.9329	0.5742	0.3185	261.5	80.45	154.3	205.6	0.278

predicting the alloying volume change. The simplest is a linear rule-of-mixture

$$V = (1 - c)V_1 + cV_2 \quad (3)$$

Here, the subscript 1 denotes the reference material, the Fe-Cr-Ni alloy, and subscript 2 denotes the alloy element, manganese. From our mass-density measurements and corroborating X-ray-diffraction measurements [5], we find $V_1 = 11.60 \times 10^{-3} \text{ nm}^3$. The volume V_2 corresponding to a manganese atom in an fcc crystal structure remains uncertain. For the α -Mn crystal structure, $V_2 = 12.21 \times 10^{-3} \text{ nm}^3$. For fcc manganese, Pauling [6] estimated $V_2 = 11.58 \times 10^{-3} \text{ nm}^3$. Studies on Mn-Cu alloys predict $V_2 = 12.59 \times 10^{-3}$ [7], 12.67×10^{-3} [8], and $13.02 \times 10^{-3} \text{ nm}^3$ [9]. We adopt $V_2 = 12.59 \times 10^{-3} \text{ nm}^3$. Then Equation 3 predicts

$$\frac{\Delta V}{cV} = 0.085 \quad (4)$$

A more realistic model, which uses both second- and third-order elastic constants, was given by Gschneidner and Vineyard [10]

$$\frac{\Delta d}{cd} = \frac{d_2 - d_1}{d_1} + 2 \left(\frac{dG}{dP} - \frac{G}{B} \right) \left(\frac{\Delta d}{d_1} \right)^2 \quad (5)$$

Here, d denotes the interatomic spacing, G the shear modulus, B the bulk modulus, and P the pressure. From Gerlich and Hart [11], $dG/dP = 1.75$, and d relates to the volume according to

$$d = (\sqrt{2}/2)a = (\sqrt{2}/2)(V/4)^{1/3} \quad (6)$$

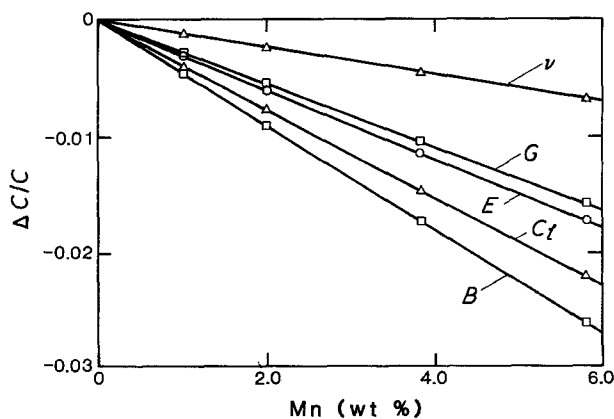


Figure 1 Compositional variation of several measured quantities: C_1 = longitudinal modulus, B = bulk modulus, G = shear modulus, E = Young modulus, ν = Poisson ratio. Temperature = 295 K.

where, a denotes the cubic unit-cell dimension, and

$$\begin{aligned} \frac{\Delta V}{V_1} &= \frac{d^3 - d_1^3}{d_1^3} \\ &= 3 \left(\frac{d - d_1}{d_1} \right) + 3 \left(\frac{d - d_1}{d_1} \right)^2 + \left(\frac{d - d_1}{d_1} \right)^3 \end{aligned} \quad (7)$$

Combining Equations 5 and 6 and using Equation 7 predicts that

$$\frac{\Delta V}{cV} = 0.091 \quad (8)$$

Thus, a simple model predicts the observed volume change.

Second, we consider the observed elastic-constant reductions caused by manganese alloying. As described elsewhere [11], a model by Eshelby predicts the elastic-constant changes arising from the volume change caused by dilatation centres

$$\frac{\Delta B}{B} = - \frac{dB}{dP} \frac{\gamma - 1}{\gamma} \frac{dV}{V} \quad (9)$$

and

$$\frac{\Delta G}{G} = - \frac{dG}{dP} \frac{B}{G} \frac{1}{\gamma} \frac{dV}{V} \quad (10)$$

where

$$\gamma = \frac{3B + 4G}{3B} = 3 \frac{1 - \nu}{1 + \nu} \quad (11)$$

From Gerlich and Hart [12], $dB/dP = 5.57$ and $dG/dP = 1.75$. Thus, on the basis of the observed

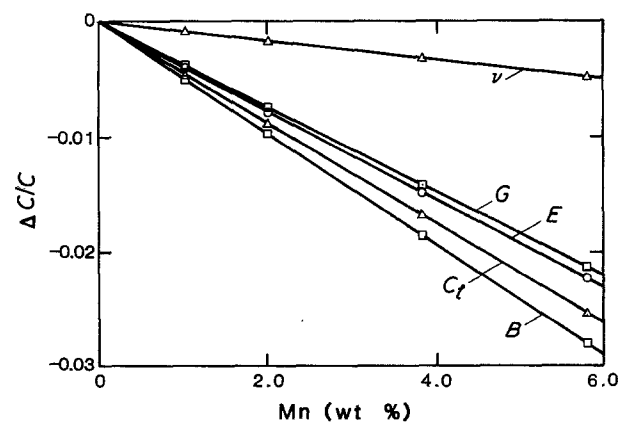


Figure 2 As Fig. 1, at 4 K.

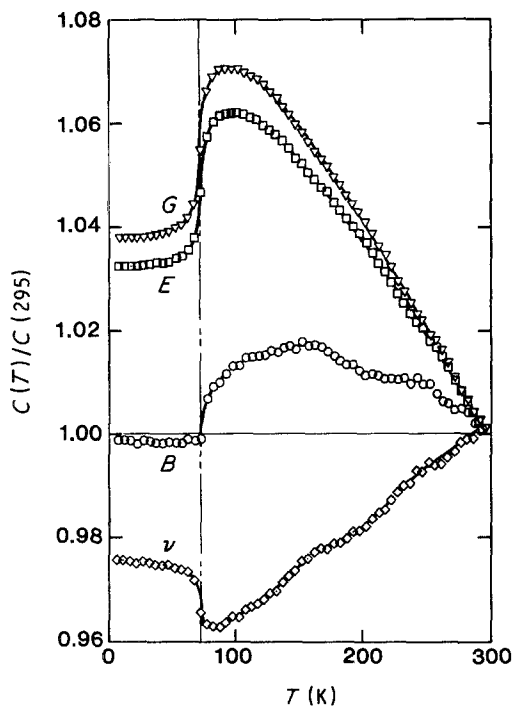


Figure 3 For the 3.85 wt % Mn alloy, variation with temperature of several measured quantities: B = bulk modulus, G = shear modulus, E = Young modulus, ν = Poisson ratio. The non-regular behaviour arises from a reversible magnetic phase transition. The broken line indicates the temperature corresponding to the cusp in magnetic-susceptibility plotted against temperature. The negative slope $d\nu/dT$ suggests further low-temperature magnetic changes. Softening of B during cooling suggests magnetic changes premonitory to paramagnetic-antiferromagnetic (Néel) transition.

volume change, these relationships predict $\Delta B/cB = -0.20$ and $\Delta G/cG = -0.21$. These predictions fall well below observation: -0.54 and -0.30 for B and G , respectively. This discrepancy, especially for B , means that a simple model based on volume change and second-order and third-order elastic constants fails to explain the observations. We conclude that other interatomic interactions occur: probably local magnetic interactions, which affect B more than G . As described below, two other observations support the hypothesis of local magnetic interactions. First, manganese raises the magnetic-transition temperature, stabilizing an ordered magnetic phase. Second, upon cooling, far above the magnetic transition, B softens before G . This suggests that as interatomic spacing

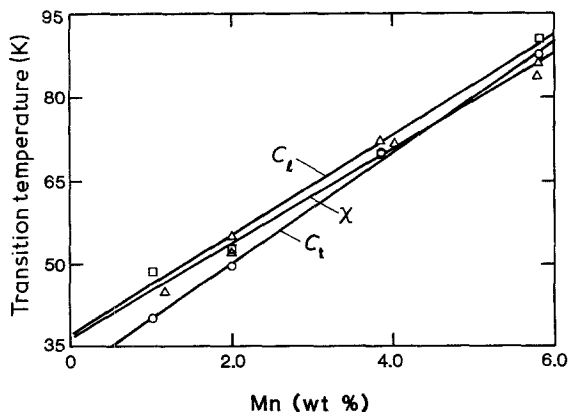


Figure 4 Manganese alloying effect on magnetic (Néel) transition temperature. χ denotes d.c. magnetic susceptibility. (○) C_1 , (□) C_2 , (△) χ .

decreases, magnetic repulsion interactions intensify, and volume increases, lowering B .

Third, we compare the 295 K and 4 K composition effects. Figs 1 and 2 show their similarity, the 4 K changes being slightly larger. (The Poisson ratio provides one exception: at 4 K, it changes less with composition.) This similarity suggests that the Mn-Fe-Cr-Ni interactions do not differ much at temperatures above and below the magnetic-transition temperature.

Fourth, we consider the cooling curves, which reproduced reversibly during heating. At the magnetic transition temperature (confirmed separately by magnetic-susceptibility measurements [4]), all the elastic stiffnesses decrease and the Poisson ratio increases. Although we did not measure the volume change associated with the magnetic transition, we suspect that this expansion during cooling may explain most of the elastic-stiffness decrease. Above, we mentioned that the bulk modulus begins to soften at temperatures well above the magnetic-transition temperature. This softening we ascribe to increased (by lattice contraction) local magnetic interactions, interactions that soften B but not G . Below the magnetic-transition temperature, all the elastic stiffnesses resume usual temperature behaviour, except for the Poisson ratio, instead of decreasing as expected, it tends to increase. We ascribe this unexpected tendency to increase as, again, showing changes in magnetic interaction, this time below the magnetic-transition temperature.

Fifth, we consider how manganese changes the magnetic-transition temperature. If manganese only increased the volume, we would expect the transition temperature to decrease, because the interacting species are farther apart. However, we observe an increase: approximately 9 K per atomic per cent manganese. Again, we suspect that increased local magnetic interactions enhance the existing tendency of the Fe-Cr-Ni alloy to order magnetically. Whether the dominant interaction is Fe-Mn, or otherwise, remains uncertain.

5. Conclusions

From this study of nominally Fe-18Cr-8Ni alloys, there emerge five conclusions:

(1) Elastic-constant changes caused by manganese alloying at 4 K strongly resemble the changes at 295 K. Except for the Poisson ratio, the 4 K results show slightly larger reductions. Thus, cooling through the magnetic phase transition produces no large changes in the manganese elastic-constant contributions.

(2) As expected from previous studies, cooling through the magnetic phase transition decreases all the elastic stiffnesses and increases the Poisson ratio. Above the magnetic phase transition, the bulk modulus begins to soften.

(3) Manganese raises the magnetic transition temperature, by a large amount: 9 K per atomic per cent manganese.

(4) A simple model based on atomic volumes and second-order and third-order elastic constants explains the volume increase.

(5) Simple models fall short by approximately one half in explaining the elastic-constant decreases. In

particular, the bulk modulus decreases more than expected. We attribute this softening to local magnetic interatomic interactions.

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