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Shock-Wave Compression of 30% Ni–70% Fe Alloys: The Pressure-Induced Magnetic Transition*

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The compressibility of 30% Ni–70% Fe (wt %) in the fcc phase is investigated from atmospheric pressure to 40 kbar with shock-wave loading techniques. The experiments are accomplished utilizing projectile impact techniques with stress profile measurements by the quartz gauge. A sharp change in compressibility indicates a second-order ferromagnetic Curie point transition at a stress of 25 kbar and a volume of 0.9807 V_0. The coefficient of Curie temperature change with pressure is found to be -5.8 ± 0.3°C kbar^{-1}. The agreement of this value with previous magnetic measurements, along with the anomalously large compressibility below the transition and the large decrease in compressibility at an elevated temperature, clearly indicates that this transition is a ferromagnetic to paramagnetic transition. Values for the change of thermal expansion and specific heat at the transition are computed from the Ehrenfest relations. These values are consistent with the magnetic character of the transition and give a complete description of the thermodynamic properties of the transition. To provide more compressibility data on various types of ferromagnetic materials, a few additional measurements are reported for Invar and 30% Ni–70% Fe in the bcc phase.

INTRODUCTION

UNUSUAL physical properties which are strongly correlated with unusual magnetic properties are characteristic of the alloys of about 30% to 40% Ni in Fe.[1] It is known that the Curie temperature and saturation magnetization of these alloys show an enormous sensitivity to pressure, reflecting a strong volumetric dependence of the magnetic interactions.[2,3] This strong pressure dependence of the magnetic order has allowed a number of investigations of the volumetric dependence of the magnetic order with the use of relatively low (5 kbar) pressures.[4] From these previous investigations it appears, as we will show, that the change in compressibility associated with the change in magnetic interactions is large enough to be readily measured in shock-wave compression experiments. Thus, a study of the thermodynamic properties of the pressure-induced magnetic transition appears promising. It is the object of this paper to report an investigation of the shock-wave compression of 30% Ni–70% Fe in the fcc phase which has resulted in the identification and determination of the thermodynamic properties of the pressure-induced ferromagnetic to paramagnetic transition. There appears to be no previous identification of a pressure-induced second-order phase transition under shock-wave compression.

BACKGROUND AND THEORY

The transition from a ferromagnetic to a paramagnetic state is normally considered to be a classic second-order phase transition; that is, there are no discontinuous changes in volume V or entropy S, but there are discontinuous changes in the volumetric thermal expansion β, compressibility k, and specific heat C_p. The relation among the variables changing at the transition is given by the Ehrenfest relations,

$$\Delta k_T = \Delta\beta(d\theta/dP), \tag{1}$$

and

$$\Delta C_p = TV\Delta\beta(d\theta/dP)^{-1}; \tag{2}$$

where Δ indicates the change occurring at the transition, k_T is the isothermal compressibility $-V^{-1}(dV/dP)_T$, and $d\theta/dP$ is the coefficient of Curie temperature change with pressure. It is clear from Eqs. (1) and (2) that a measurement of Δk_T and $d\theta/dP$ will result in a complete description of the thermodynamic properties of the transition.

The alloys of from 30% to 40% Ni in iron are noted for their unusual volumetric behavior. For example, it is well known that the thermal expansion of these alloys is anomalously low, with the Invar composition (36% Ni) having a thermal expansion close to zero at room temperature. Further, the atmospheric pressure compressibilities are anomalously large while the atomic lattice spacing and density data show strong departures from Vegard's law in this same composition range.[5,6]

For alloys containing up to about 27% Ni in Fe, the equilibrium phase at room temperature is bcc. However, in the neighborhood of 30% Ni either the fcc or bcc phases can be obtained at room temperature as the result of various heat treatments.[7] For nickel concentrations greater than 30%, the structure is fcc. Hence, the unusually large volumetric phenomena are characteristic of the fcc phase.

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[1] Compositions are given in wt % unless otherwise specified.

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[3] J. S. Kouvel and R. H. Wilson, J. Appl. Phys. **32**, 435 (1961).

[4] J. S. Kouvel, in *Solids Under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill Book Company, Inc., New York, 1963).

[5] E. A. Owen, E. L. Yates, and A. H. Sully, Proc. Phys. Soc. (London) **49**, 315 (1937).

[6] A summary of physical and mechanical property data for Invar is given in: W. S. McCain and R. E. Maringer, "Mechanical and Physical Properties of Invar and Invar-Type Alloys," DMIC Memorandum 207 (August, 1965), Defense Metals Information Center, Battelle Memorial Institute.

[7] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 677–684.

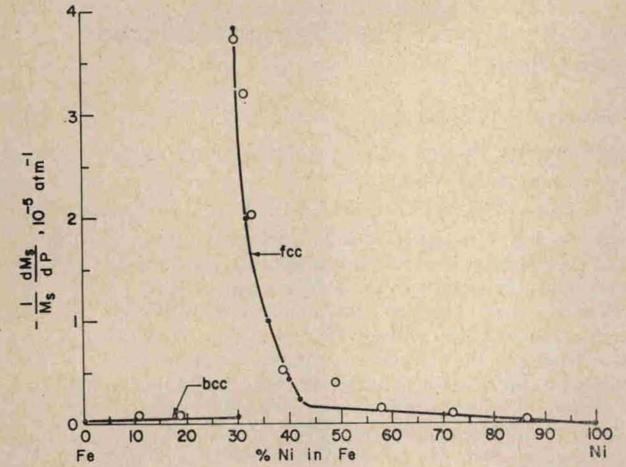

FIG. 1. Pressure dependence of the saturation magnetization of the Fe–Ni alloy system. The filled circles are data from Ref. 3 and the open circles are data from Ref. 8. Compositions are in atomic percent.

The pressure sensitivity of the magnetic properties of the Invar type alloys is indicated by extensive measurements[3] of the coefficient of saturation magnetization change with pressure $M_s^{-1}dM_s/dP$ for various compositions as shown in Fig. 1.[8] The exceedingly large values in the 30%–40% Ni range are evident and much in excess of the values for iron and nickel. The 30% Ni composition in the fcc phase is the most sensitive to pressure while this composition in the bcc phase is insensitive to pressure although strongly ferromagnetic.[3]

The change in compressibility expected if the transition occurs can be estimated from Eq. (1), since values for $d\theta/dP$ have been measured at low pressure and a value can be estimated for $\Delta\beta$. The value for $d\theta/dP$ measured by Patrick[2] for fcc 30%Ni–70%Fe is -5.7°C kbar^{-1} while the value for the bcc phase is about -0.3°C kbar^{-1}. The Curie temperature for the fcc alloy is 155°C while that for the bcc alloy is about 700°C.[4] On the basis of these values the expected behavior if the transition occurs is a large, easily detected change in compressibility at a pressure of 23 kbar for the fcc alloy and an anomalously large compressibility below the transition. On the other hand, the compressibility of the bcc alloy should exhibit normal behavior in this pressure range.[9] Hence, a measurement of the compressibility of fcc and bcc 30% Ni–70% Fe alloys to pressures of about 40 kbar should result in definite conclusions concerning the transition and the effect of magnetic interactions on shock-wave compressibility. Selection of the alloy 30% Ni–70% Fe for this investigation was based upon this unique combination of properties in the two phases and the exceptionally large coefficient of Curie temperature change with pressure for the fcc phase.

Plane shock-wave loading experiments yield precise stress–volume measurements; hence, they are a convenient method for observing the expected transition. A recently developed gun with essentially continuous control on the stress imparted to a sample[10] ($\sim$2 kbar increments) coupled with the excellent time resolution available with the quartz gage[11] provide a sound basis for measurements in this pressure range.

Curran[12] has pointed out that under certain unusual conditions the second-order phase transition might cause a cusp in the stress–volume relation resulting in a multiple wave structure as is the case for a first-order transition. His shock-wave compression measurements on Invar (36%Ni–64%Fe) showed large compressibilities in the low stress region but no distinct transition. In order to verify his results, we have also performed a few experiments on Invar.

EXPERIMENTAL PROCEDURE

Shock-wave loading is accomplished by the planar impact in vacuum of two flat disks. The stationary specimen disk is mounted on the muzzle of a compressed gas gun and the other disk is attached to the impact face of a projectile which is accelerated to various velocities by the gun. Shock-wave velocity measurements and measurements of the shock-wave stress–time profile with the quartz gage at a plane some distance from the impact surface are sufficient to compute the stress–volume relation for the shocked sample from the conservation of mass and momentum relations.[13] Precision is maintained in all alignment tolerances such that the "tilt" of one surface relative to the other at impact is typically 5×10^{-4} rad. A schematic of this method of performing the shock-wave experiment is shown in Fig. 2.

The gun experiment permits an additional measurement to those possible when high-explosive loading is

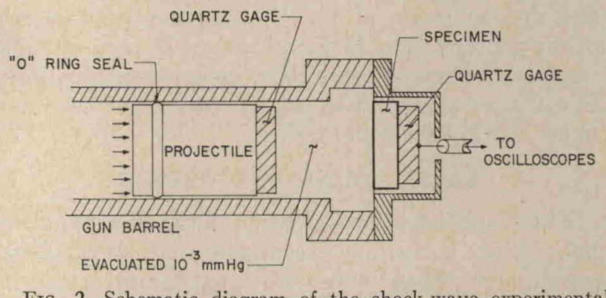

FIG. 2. Schematic diagram of the shock-wave experimental arrangement. In some of the experiments, the quartz gauge on the projectile is replaced by a facing of the specimen material.

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