elastic limit, whereas the dashed line shown for the fcc alloy indicates the stress region for which some strain hardening is indicated from the stress profiles. It is readily apparent that below 25 kbar the fcc alloy shows a much larger compressibility than the bcc alloy.

ANALYSIS

The compressibility of the fcc alloy shows a large, well-defined change at 25 kbar, clearly indicating the expected behavior for a second-order phase transition. The anomalously high value of the compressibility for the pressure-sensitive fcc alloy is demonstrated in the comparison of compressibilities of various ferromagnetic iron alloys in Table II.[17–19] The fcc 30% Ni alloy as well as the Invar alloy have compressibilities which are far in excess of the normal values for the ferromagnetic iron alloys whose magnetic properties are not pressure sensitive. Further, for stress in excess of the stress required to induce the transition to the nonmagnetic state, the compressibilities of both 30% Ni and Invar have a normal value. Invar does not show a well-defined transition, but its roughly analogous behavior to that of the fcc 30% Ni alloy shows that magnetic effects are responsible for the pressure induced change in compressibility.

TABLE II. Compressibilities of various iron alloys.

Material	$-(1/V)(\Delta V/\Delta P)$, 10^{-4} kbar^{-1} Shock wave compression	Low signal adiabatic
Pressure-sensitive ferromagnetic iron alloys		
30% Ni 70% Fe, fcc	8.6[a]	8.97[a]
36% Ni 64% Fe, fcc	8.8[a]	8.9[b]
Pressure-insensitive ferromagnetic iron alloys		
30% Ni 70% Fe, bcc	6.0[a]	6.6[c]
Armco Fe, bcc	6.4[d]	5.93[e]
30% Ni 70% Fe, fcc. Stress range above transition stress	5.8[a]	···
36% Ni 64% Fe, fcc. Stress range above transition	5.0[f]	···
30% Ni 70% Fe, fcc. Elevated temperature (130°C)	6.4[g]	···

[a] As determined in the present investigation.
[b] Computed from Young's modulus and Poisson's ratio as given in Ref. 6.
[c] As given by Ref. 17.
[d] Data from Ref. 18. Stress range from 40 to 55 kbar.
[e] Reference 19.
[f] Data from Ref. 12. Stress range from 70 to 110 kbar.
[g] As determined in the present investigation. The computation assumes that the Hugoniot elastic limit does not change with temperature; thus, this value is somewhat more uncertain than the other values.

To further clarify the role of magnetic effects on compressibility, a shock compression experiment was performed on an fcc 30% Ni sample whose initial temperature was raised to 130°C. As is shown in Table II, the compressibility was found to decrease to a value consistent with the nonmagnetic compressibility. Thus, the sharp change in compressibility, the critical values for the transition, and the magnitudes of the compressibility under the various conditions give a clear demonstration that a second-order magnetic transition has been observed and we will proceed with a quantitative analysis of the transition.

PROPERTIES OF THE TRANSITION

The experiments result in an explicit measure of the change in the shock-wave compressibility which occurs at 25 kbar. For the small compressions involved (2% at 25 kbar), the shock-wave compression is adiabatic to a very close approximation. Thus, the isothermal compressibility Δk_T can be computed from the thermodynamic relation between adiabatic and isothermal compressibilities.[20] Further, from the pressure and temperature of the transition, the coefficient $d\theta/dP$ can be computed. The evaluation of both Δk_T and $d\theta/dP$ allow the change in thermal expansion and specific heat to be computed from Eqs. (1) and (2), and a complete description of the properties of the transition is then obtained.

The temperature at the transition is the initial temperature[21] of the sample plus the shock-wave heating which occurs. This temperature rise is only 3°C up to the transition,[22] and is small enough that uncertainties in the change in Curie temperature are principally due to the measurement of Curie temperature at atmospheric pressure. Thus, the Curie temperature is lowered from 155°C to 25°C due to the stress of 25 kbar.

The small but significant component of shear stress that is associated with the elastic compression results in a stress configuration which is not hydrostatic. Thus, the shock-wave experiment measures a longitudinal component of stress rather than the pressure of the transition. Belov has shown that shear stress does not change the Curie temperature or saturation magnetiza-

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[20] $\Delta k_T=\Delta k_s[1+T(\beta_1\gamma_1-\beta_2\gamma_2)]$, where Δk_s is the change in adiabatic compressibility at the transition and γ is the Grüneisen ratio. The subscripts 1 and 2 refer to values in the low-pressure and high-pressure phases, respectively. β_1 is taken as zero in agreement with data to be shown later, β_2 is taken as 4.4×10^{-5} °C^{-1} and C_P is taken as 1.2×10^{-1} cal g^{-1} °C^{-1}.
[21] The experiment is conducted in a temperature-controlled room at 22°C.
[22] The temperature is computed as $T_s=T_0(V_0/V)^\gamma$ where γ is the appropriate Grüneisen's ratio which is computed from the relation $\gamma=\beta C_P/k_sV$. As is shown later, our best estimate is that γ decreases from its room-temperature value, 0.85, to zero at a stress just below the transition due to the decrease in thermal expansion. Since the volume change and temperature rise are small, we choose γ as 0.43, a mean value over the pressure range. This is admittedly crude, but the difference between this calculation and a more sophisticated analysis is insignificant.

TABLE III. Values for the coefficient of Curie temperature change with pressure, $d\theta/dP$.

Patrick[a]	-5.7 ± 0.2°C kbar^{-1}
Belov[b]	-5.4
Kaneko[c]	-3.2
Samara[d]	-5.5
Present work	-5.8 ± 0.3

[a] Curie temperature shift determined by susceptibility measurements. Maximum pressure 5 kbar. Ref. 2.
[b] Calculated from volume magnetostriction measurements at atmospheric pressure, Ref. 23.
[c] Curie temperature shift determined by magnetization-temperature measurements. Maximum pressure 3 kbar. Ref. 25.
[d] Curie temperature shift determined by susceptibility measurements. Maximum pressure 25 kbar. Ref. 26.

tion of these alloys.[23,24] His values for $d\theta/dV$ measured in uniaxial stress (which results in a large shear stress) are the same as those obtained hydrostatically. Thus, it is the volume, $0.9807V_0$, which is characteristic of the transition. To compare our values to the previous hydrostatic pressure values, an equivalent pressure must be computed from our observed value for the volume at the transition. The equivalent pressure is computed from our measured compressibility and the volume change to induce the transition. This yields a value of 22.6 kbar for the equivalent pressure of the transition. From this value of the equivalent pressure and the temperature change induced by this pressure, the value of $d\theta/dP$ is calculated to be -5.8°C kbar^{-1}. Our value is an average value over the entire pressure range. As shown in Table III,[25,26] this value is in good agreement with most of the previous investigators; therefore, we conclude that $d\theta/dP$ is constant over the entire pressure range encountered.

The thermodynamic description of the transition can now be completed since we now have a measure of both Δk_T and $d\theta/dP$ and can calculate $\Delta\beta$ and ΔC_p from Eqs. (1) and (2) with results as summarized in Table IV. Thus, these experiments provide a complete description of the thermodynamic properties of the transition.

DISCUSSION

The value of the change in thermal expansion coefficient accompanying the transition is considerably larger than that obtained when the transition is thermally induced at atmospheric pressure. That is, our value for the thermal expansion at 22°C and atmospheric pressure is 3.0×10^{-5} °C^{-1} and for temperatures above the transition temperature the value is 5.1×10^{-5} °C^{-1} which is a normal paramagnetic value for alloys in this composition range. Since the change in thermal expansion which occurs at the pressure induced transition is $+4.7\times10^{-5}$ °C^{-1}, a normal value for the thermal expansion in the high-pressure paramagnetic state implies that in the low-pressure ferromagnetic state the thermal expansion coefficient decreases strongly with pressure to a value close to zero immediately before the transition.

Although there are no direct measurements of the thermal expansion coefficient of this alloy at various pressures, compressibility vs temperature measurements have been made.[27] From these compressibility data and thermodynamic identity $\partial\beta/\partial P=-\partial k/\partial T$ the initial slope of the thermal-expansion–pressure relation can be computed at atmospheric pressure. This initial slope is found to be $+1.7\times10^{-6}$ °C^{-1} kbar^{-1} which is in contradiction to the behavior we have inferred from our high-pressure measurements. However, the extrapolation of initial slopes at atmospheric pressure to high pressures where there are large changes in the magnetic interactions is clearly an uncertain procedure. Thus, the most likely behavior of the thermal expansion coefficient with pressure is an initial small increase followed by a continual decrease in slope until a large negative slope is obtained.

The thermal expansion data appear to be applicable to an interpretation of the physical nature of the magnetic interactions and their change with pressure. Kouvel and Wilson,[3] and Kondorsky and Sedov[28] have postulated that the unusual volumetric behavior of the magnetic interactions is a result of a mixed ferromagnetic, antiferromagnetic coupling. The iron–iron interactions are thought to be antiferromagnetic whereas the Ni–Ni and Ni–Fe interactions are ferromagnetic. Weiss[29] has discussed the possibility that fcc iron has two electronic states and has calculated the thermal-expansion–temperature relation predicted on this basis. It may be possible to examine such physical models on the basis of

TABLE IV. Characteristics of the pressure-induced magnetic transition in fcc 30% Ni–70% Fe.

Specific volume	$0.9807\ V_0$
Temperature (°C)	25
Equivalent pressure (kbar)	22.6
$d\theta/dP$ (°C kbar^{-1})	-5.8 ± 0.3
Δk_T (kbar^{-1})	$-2.72\pm0.05\times10^{-4}$
ΔC_p (cal g^{-1} °C^{-1})	$-7.2\pm0.7\times10^{-3}$
$\Delta\beta$ (°C^{-1})	$+4.7\pm0.5\times10^{-5}$

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