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Temperature Dependence of Magnetovolume for Ni–Cr Alloys Near the Critical Composition for Magnetism[1]

T. F. Smith,[2] A. B. Kaiser,[3] and G. K. White[4]

Measurements of the low-temperature thermal expansion coefficient, α, of Ni–Cr alloys close to the critical concentration, x_c, for the ferromagnetic regime may be represented in the form $\alpha = A + BT + CT^3$. The value for A increases in magnitude as x_c is approached and abruptly changes sign at x_c, being positive in the paramagnetic alloys and negative in the ferromagnetic alloys. Further measurements are reported that support a qualitative description proposed to account for the sign change in A, which is based upon a correspondence between the magnetovolume and the magnitude of the ordered magnetic moment and the moment fluctuation associated with the magnetic transition.

KEY WORDS: magnetism; Ni–Cr alloys; thermal expansion.

1. INTRODUCTION

It has been known for many years that materials with magnetic behavior associated with the border between ferromagnetism and paramagnetism are characterized by a low-temperature specific heat capacity, C_p, that may be represented by

$$C_p = A + BT + CT^3 \tag{1}$$

where the linear and cubic temperature terms are electronic and lattice contributions, respectively, and A is a magnetic contribution, which is positive

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[2] Department of Physics, Monash University, Clayton, Victoria 3168, Australia.

[3] Department of Physics, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand.

[4] Division of Applied Physics, CSIRO, P.O. Box 218, Lindfield N.S.W. 2070, Australia.

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in both the ferromagnetic and the paramagnetic states [1, 2]. More recently, there have been reports [3–5] of the representation of the linear thermal expansion coefficient, α, with the same form of temperature dependence as in Eq. (1). However, here the sign of the constant magnetic term depends upon the magnetic state, being positive in the paramagnetic regime and negative in the ferromagnetic. Furthermore, the magnetic contribution is significantly stronger in the thermal expansion, resulting in more marked "upturns" or "downturns" in α/T compared with C_p/T.

Discussions of the "constant" term in the specific heat capacity have generally been divided between descriptions based on spin fluctuations [6] and those based on superparamagnetic clustering [1]. Although some experimental data [7, 8] are more readily accounted for by the cluster model, the question as to role of spin fluctuations in the observed low-temperature specific heat capacity is unresolved.

Generally, a loss of magnetic moment results in a decrease in volume. However, in the event that the increase in the internal energy due to excitation of the magnetic spins is large, the volume may increase [9]. With the absence of any detectable discontinuity in the specific heat capacity at the ferromagnetic ordering temperature for Ni–Cr alloys close to the critical composition of ~12 at% Cr [3], it is concluded that the change in the magnetic contribution to the internal energy is negligible. Thus, changes in the magnetovolume will be related to the temperature dependence of the magnetization and may be expressed [9, 10] as

$$\omega_M(T) \simeq C\langle M^2(T)\rangle \tag{2}$$

where $\omega_M(T) \equiv \Delta V/V$ is the fractional volume change resulting from the change in the mean-square local amptitude of the magnetization, $\langle M^2(T)\rangle$, and C is the (positive) magnetoelastic coupling constant divided by the bulk modulus.

It has been recently proposed [11] that the magnetic constant term in the thermal expansion coefficient, and its change in sign, can be readily accounted for using Eq. (2) by extending the spin fluctuation model of Moriya and Usami [12]. When the energies of the ferromagnetic and paramagnetic states are close, $\langle M^2(T)\rangle$ is decreased by low-energy thermal excitations from the ferromagnetic ground state but increases with spin excitation from the paramagnetic ground state. If we take $\langle M^2(T)\rangle$ as increasing approximately linearly with temperature in paramagnetic systems (except at very low temperatures), as in the calculation of Moriya [13], we deduce a constant positive contribution to the thermal expansion coefficient, as observed. This magnetic anomaly should be largest near the critical composition for ferromagnetism where the spin fluctuation effects are largest. It would be expected to reverse in sign in the ferromagnetic state [11] because the low-energy excitations would then be mainly paramagnetic-like states of lower moment.

In this paper we present new thermal expansion measurements for Ni and Ni–Cr alloys containing 3, 6, and 11.2 at% (nominal) Cr that strengthen the argument for the excitation of low-energy spin fluctuations being responsible for the sign reversal of the magnetic anomaly.

2. EXPERIMENTAL DETAILS

2.1. Alloy Preparation and Characterization

The Ni–Cr alloys with nominal compositions of 3, 6, and 11.2 at% Cr examined in this study were prepared following the procedure described by Simpson and Smith [3]. Appropriate amounts of Ni (99.99% pure) and Cr (99.99% pure) were melted, cut, and remelted eight times in an arc furnace under high-purity argon. The resulting ingots were then heat-treated under flowing argon at 1300°C for 36 h and furnace cooled.

The ingots were spark-cut to produce roughly cylindrical samples, 9 mm in diameter and 34 mm in length. The end faces of these samples were lapped and polished parallel within 10^{-4} rad.

A microscopic analysis of the alloy composition was made for the nominal 11.2 at% Cr alloy prepared for these measurements and the nominal 11.0 at% Cr studied previously [3]. This analysis gave 11.3 ± 0.1 at% Cr for the nominal 11.2 at% Cr sample in the present study and 11.5 ± 0.1 at% Cr for the previous nominal 11.0 at% Cr sample.

The temperature dependence of the AC susceptibility for a sample spark-cut from an end piece from the nominal 11.2 at% ingot indicated a magnetic transition spread over the temperature range 13–35 K. A transition temperature of 6.9 ± 0.3 K was observed for the nominal 11.0 at% sample [3].

The magnetic ordering temperature for alloys close to the critical concentration is strongly dependent upon heat treatment and composition [3]. The microprobe analysis and the AC susceptibility measurements are consistent with the earlier nominal 11.0 at% Cr sample being higher in chromium concentration than the present nominal 11.2 at% Cr sample. The pure nickel sample was that for which expansion measurements have been reported [14].

2.2. Thermal Expansion Measurements

The thermal expansion measurements were made in a three-terminal capacitance dilatometer, the design and operating procedure of which have been described [15].

3. EXPERIMENTAL DATA

The thermal expansion data are shown in the form of a plot of α/T versus T^2 in Fig. 1. The plots for the Ni and the 3 and 6 at% Cr alloys show no sign of curvature and the data are well represented by least-squares fitting to the normal linear and cubic temperature terms.

The α/T data for the nominal 11.2 at% Cr alloy exhibit the marked "downturn" observed previously [3] for ferromagnetic Ni–Cr alloys close to the critical composition. These data were least-squares fitted to the temperature dependence given in Eq. (1).

Figure 1 also includes values of α/T measured previously [3] for a nominal 11.0 at% Cr alloy. The inflection at about 7 K corresponds to the magnetic ordering temperature. These data were previously fitted to the temperature dependence of Eq. (1) for $T < 5$ K, i.e., the *ferromagnetic* state.

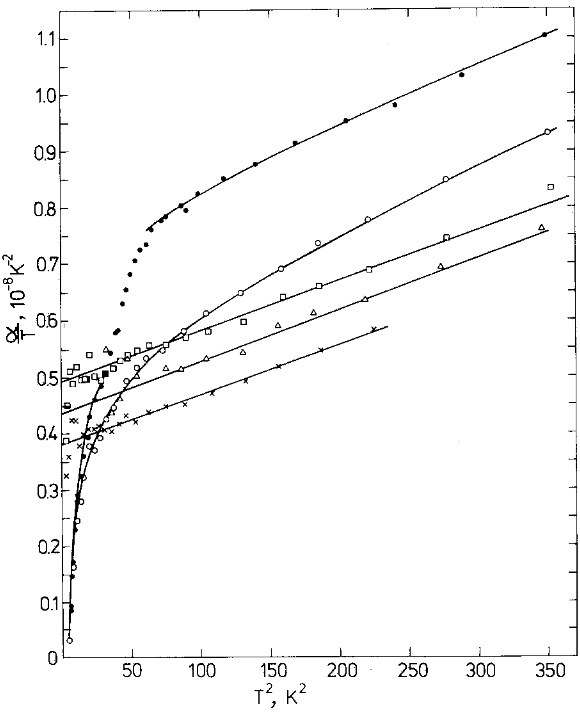

Fig. 1. Variation of α/T as a function of T^2 for Ni–Cr alloys. The symbols distinguish the chromium content, expressed as nominal atomic percentage, as follows: ×, 0; △, 3; □, 6; ●, 11; ○, 11.2.

A fit has now been made for the *paramagnetic* state over the temperature range 8 to 20 K. This fit also gives a negative value for the constant term.

The values for the fitting parameters are listed in Table I and are plotted as a function of nominal chromium composition in Fig. 2 along with values from the earlier work [3]. Although plotted at the nominal compositions of 11.0 and 11.2 at% Cr, the microprobe analysis and the magnetic susceptibility data indicate a higher actual chromium content in the nominal 11.0 at% alloy. The fitting parameters for both the ferromagnetic and the paramagnetic states of the nominal 11.0 at% alloy are shown. It is noted that there is relatively little difference between the two sets.

The present measurements confirm the abrupt nature of the changes that occur in the magnetic (constant) and electronic (linear) contributions to the thermal expansion and their association with the transition from the ferromagnetic to paramagnetic regime.

The shaded regions on the vertical axis in Fig. 2 indicate the values for B and C determined previously for the nickel sample [14].

To emphasize the changes in the temperature dependence of the magnetovolume associated with the ferromagnetic–paramagnetic transition, values of $\alpha_a - \alpha_{Ni}$, where α_a and α_{Ni} are the expansion coefficients for the alloy and pure Ni, respectively, have been calculated and are shown in Fig. 3. This plot clearly illustrates the positive and negative contributions to the expansion coefficient for the alloys.

In the case of the 3 at% (not shown) and 6 at% alloys $\alpha_a - \alpha_{Ni}$ is linear in temperature, extrapolating to zero at zero temperature. In addition to the positive or negative contribution, $\alpha_a - \alpha_{Ni}$ for the higher

Table I. Least-Squares Fitting Parameters for the Linear Expansion Coefficient Fitted to the Temperature Dependence Given in Eq. (1)

Alloy (at% Cr)[a]	A (10^{-8} K^{-1})	B (10^{-8} K^{-2})	C (10^{-11} K^{-4})
0	0	0.380	0.881
3	0	0.436	0.929
6	0	0.492	0.883
11[b]	−1.619	0.770	0.74
11[c]	−0.757	0.797	1.0
11.2	−1.209	0.612	1.1

[a] Nominal composition.
[b] Data from Ref. 3 fitted for $T < 5$ K.
[c] Data from Ref. 3 fitted for $8\ \mathrm{K} < T < 20$ K.

concentration alloys generally has a stronger temperature dependence. The requirement that $\alpha_a - \alpha_{Ni} \to 0$ as $T \to 0$ implies that $\alpha_a - \alpha_{Ni}$ for the ferromagnetic alloys must pass through a negative minimum at a temperature below 2 K. Evidence for this is seen for the 9.8 at% alloy.

$\alpha_a - \alpha_{Ni}$ for the 9 at% alloy has a distinct inflection between 6 and 8 K which appears to be associated with a transition between a region of

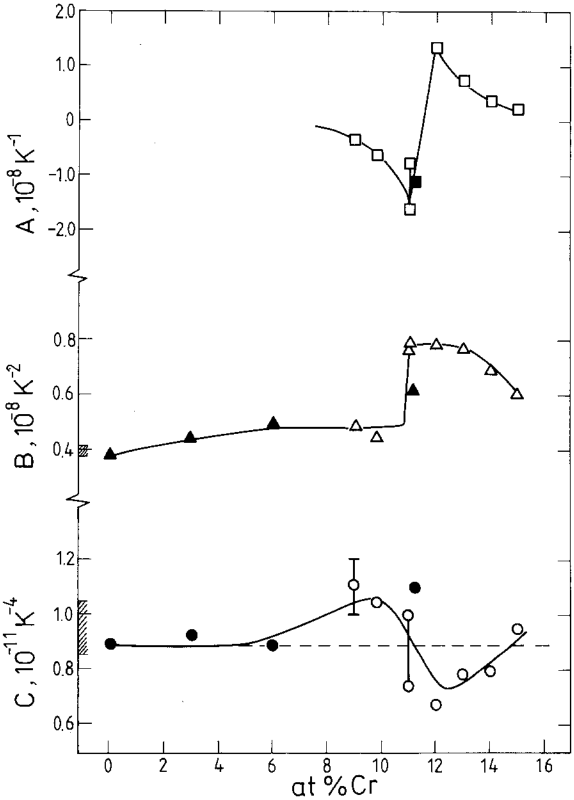

Fig. 2. Least-squares fitting coefficients for fits to $\alpha = A + BT + CT^3$ as a function of nominal Cr composition. Filled symbols represent present measurements. Open symbols are taken from Ref. 3. The shaded regions represent the values and associated uncertainties for previous measurements for nickel [14]. The level of uncertainty is indicated by the bars for C and for A and B by the size of the symbol for A and B. In the case of the nominal 11.0 at% Cr alloy the lower symbols are for the fit for $T < 5$ K (ferromagnetic state), and the upper symbols are for the fit for $8 < T < 20$ K (paramagnetic state).

relatively low temperature dependence to one in which the temperature dependence is stronger and similar to that for the higher-concentration alloys.

The closeness of the fitting parameters in the ferromagnetic and paramagnetic states for the nominal 11.0 at % alloy is evident in the temperature dependence of $\alpha_a - \alpha_{Ni}$ with the effect of the magnetic transition being to introduce a displacement of $\sim 1 \times 10^{-8}$ K^{-1}.

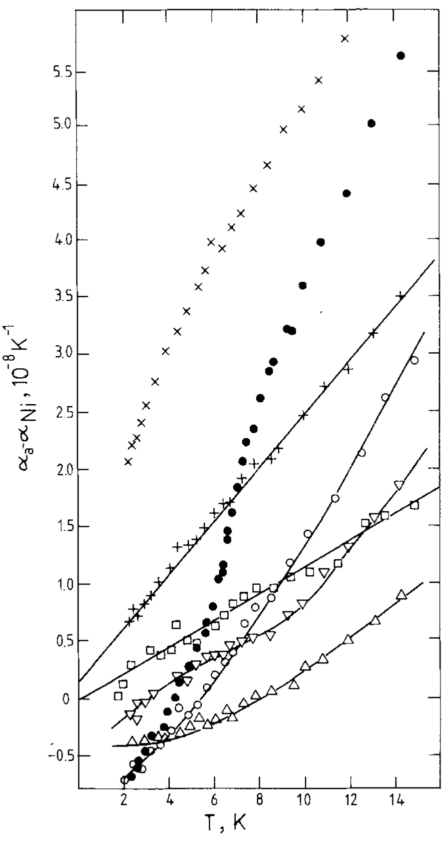

Fig. 3. The calculated temperature dependence of Ni–Cr alloy linear expansion coefficients, α_a, relative to pure nickel α_{Ni}. The symbols distinguish the chromium content, expressed as nominal atomic percentage as follows: +, 15; ×, 12; ○, 11.2; ●, 11.0; △, 9.8; ▽, 9; □, 6.

4. DISCUSSION

It has recently been suggested [11] that the approximately linear temperature dependence (at low temperature) of the magnetovolume, implied by the "constant" term in the linear thermal expansion coefficient, and its abrupt change in sign at the critical composition for ferromagnetism are convincing evidence of the influence of amplitude spin fluctuations on the magnetovolume. The lack of any evidence for a constant term in the low-temperature expansion of pure Ni and the 3 and 6 at% alloys strongly supports its association with the critical composition for magnetism, in agreement with this picture. While clustering effects could produce enhancements of specific heat, it is not clear how they could produce the reversal in the sign of the expansion anomaly.

The sharp increase in B, the coefficient of the linear temperature term, accompanying the transition from the ferromagnetic to the paramagnetic regime also indicates a significant T^2-dependent contribution to the magnetovolume in the ferromagnetic state. Such a temperature dependence is consistent with the decline in uniform magnetic moment due to single-particle excitations in the itinerant electron model for magnetism (the Stoner model) [16] and due to spin fluctuations in the model of Lonzarich and Taillefer [17]. Noting that the increase in B actually occurs *before* the ferromagnetic state is destroyed, we are led to the conclusion that the nature of the ferromagnetic ground-state excitation is changing in a manner consistent with low-energy amplitude spin fluctuations being responsible for the magnetic behavior close to the critical composition.

Furthermore, we note that the fit for the nominal 11.0 at% alloy above T_C still yields a negative value for the constant term, although it is a less significant component of the expansion in this temperature range. We see from Fig. 1 that the increase in expansion at T_C appears to have a tail extending into the paramagnetic region, probably representing the decay of vestigial ferromagnetic short-range order in the form of low-energy spin fluctuations as temperature increases above T_C. For the nominal 11.2 at% alloy, with its broad transition, there appears to be a smooth decay of ferromagnetic order, with no discontinuity associated with a sharp transition.

The data shown in Fig. 2 for the coefficient C of the T^3 term in the expansion suggest that there could be a magnetic effect in this coefficient as well near the critical composition, but any effect is small.

In the zero temperature limit, the anomalous magnetic expansion term we have represented by a constant must in fact disappear. As mentioned, the upward curvature of the 9.8 at% alloy data in Fig. 3 may be an indication of this disappearance, as well as the downward curvature of the

12 at% alloy data for the lowest temperatures. For the new nominally 11.2 at% sample, as well as for the previous 11.0 at% sample, the relatively large size of the negative "constant" term means that a rather sharp minimum in their expansion relative to Ni is anticipated somewhere below 2 K.

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