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Thermodynamic Studies and Magnetic Ordering of Ni–Cr Alloys Close to the Critical Composition

M. A. Simpson and T. F. Smith

Department of Physics, Monash University, Clayton, Vic. 3168.

Abstract

We report measurements of the specific heat capacity and the thermal expansion for Ni–Cr alloys in the vicinity of the magnetic ordering temperature T_M and at lower temperatures. No evidence of a contribution due to the magnetic ordering is found in the specific heat capacity and only the indication of a small contribution in the thermal expansion near to T_M for an Ni 11 at.% Cr alloy. A significant contribution of magnetic origin is seen for both quantities at lower temperatures. Values for the magnetic Grüneisen parameter γ_M^T are derived from the specific heat capacity and thermal expansion data and compared with values of $d \ln T_M / d \ln V$ obtained from direct measurements of dT_M/dP. Both γ_M^T and $-d \ln T_M / d \ln V$ are large and negative for weakly ferromagnetic alloys but differ numerically, whereas for paramagnetic alloys γ_M^T is large and positive.

1. Introduction

It has long been known that there is a large magnetic contribution to the low temperature heat capacity of alloys made by diluting nickel with sufficient non-magnetic material to the point where ferromagnetism vanishes. It is a common feature of such solid solutions that the low temperature heat capacity may be represented by

$$C_p = A + BT + CT^3 \qquad (1)$$

for compositions near the critical solute concentration for magnetism (Hahn and Wohlfarth 1968; Gregory and Moody 1975).

Attempts to explain this anomalous 'constant' contribution to the heat capacity have been generally divided between models based upon many-body interactions (paramagnons) or superparamagnetic clustering (Hahn and Wohlfarth 1968). In the former case the magnetic heat capacity C_M is predicted to vary as $T \ln T$ in the low temperature limit (Makoshi and Moriya 1975). However, experimental measurements in zero and applied magnetic fields have revealed Schottky-like maxima in C_M (Falge and Wolcott 1971; Aitken *et al.* 1981) which may be more readily explained in terms of superparamagnetic clusters.

A number of models based upon superparamagnetic clusters have been proposed. Schröder (1961) and Livingston and Bean (1961) considered the magnetism near the critical concentration to be confined to Ni-rich regions acting as effectively independent superparamagnetic particles whose energy levels are split by internal anisotropy fields. Another view relates the magnetic ordering to spin glass freezing (Ododo and Coles 1977; Aitken *et al.* 1981). Falge and Wolcott (1971) have also argued

that the magnetic heat capacity in their study of Ni–Cu alloys could result from a cooperative ordering of the magnetic clusters.

The heat capacity and the thermal expansion are closely related thermodynamic quantities. From elementary thermodynamics, the coefficient β of volume thermal expansion is related to the pressure dependence of the internal energy, whereas the heat capacity C_p is the temperature derivative of the internal energy. If there is only one dominant characteristic energy E, the heat capacity and the thermal expansion are proportional to one another (see e.g. White 1962), and

$$\gamma_E = \beta V B_T / C_p, \tag{2}$$

where B_T is the isothermal bulk modulus, V is the molar volume and γ_E is a constant (the thermodynamic Grüneisen parameter) equal to $-\partial \ln E / \partial \ln V$.

In the case of a system which orders magnetically at a temperature T_M, where T_M is directly proportional to E, a magnetic Grüneisen parameter is given by

$$\gamma_M = -\partial \ln E / \partial \ln V = -\partial \ln T_M / \partial \ln V. \tag{3}$$

For convenience, we shall represent the thermodynamic Grüneisen parameter by γ_M^T and the one derived from pressure measurements by γ_M.

Measurements of T_M as a function of pressure have been made for a number of weak magnetic systems (Schilling 1979; Wagner and Wohlfarth 1981), but relatively little attention has been directed towards their expansion behaviour. Thermodynamic Grüneisen parameters have been determined for some spin glass and Kondo systems (see Smith 1981 for a review and individual references), but a comparison between the thermodynamic γ_M^T and γ_M derived directly from the pressure dependence of the glass temperature has only been possible for **Cu**Mn and **Ag**Mn. Reasonable agreement was found between the two parameters.

Although there have been numerous studies of the heat capacity for alloy systems close to the critical composition for ferromagnetism, there is only one published report of a measurement of thermal expansion (Kortekaas and Franse 1977). While the magnetic contribution in these measurements for Ni_3Al and Ni–Pt alloys is not specifically identified, there is nevertheless clear evidence of a change in the sign of the low temperature expansion coefficient on passing from the ferromagnetic to paramagnetic regime.

The theoretical interpretation of the magneto-volume effects in these weak magnetic systems has centred around a debate between the relative merits of a unified theory based upon spin fluctuations (Moriya 1979; Moriya and Usami 1980) and the Stoner itinerant theory of ferromagnetism (Wohlfarth 1980, 1981). No descriptions of magneto-volume effects have been published for the superparamagnetic cluster models.

In this work, we present measurements of the coefficient of linear expansion and specific heat capacity at low temperatures and the pressure dependence of the Curie temperature T_M for Ni–Cr alloys in the Cr concentration range where T_M goes to zero.

2. Experimental Method

(a) *Specimen Preparation*

Two separate series of specimens were made for this work. Specimens for heat capacity and thermal expansion measurements were prepared by arc-melting together

weighed amounts of 5N Ni rods (Koch–Light Laboratories) and 5N Cr flake (Halewood Chemicals Ltd). The ingots were then rolled into thin strips between Mo sheet, and the strips were cut up and remelted to ensure homogeneity. The resulting ingots were machined to 9·52 mm diameter to fit into the holder in the heat capacity apparatus and then heat-treated in flowing purified Ar at 1300°C for 36 hours and furnace cooled. We note that in previous investigations (Besnus *et al.* 1972; Tange *et al.* 1981) samples were water quenched from 900°C. We have found that this procedure raised the T_M for an 11·5 at.% Cr sample from below 4 K to 11·4 K and reduced the sharpness of the a.c. susceptibility peak. Tranchita and Claus (1978) have reported similar behaviour in Ni–Cu alloys. Small square section bars with dimensions $2{\cdot}8 \times 2{\cdot}8 \times 8{\cdot}4\ mm^3$ were cut from each end of each ferromagnetic specimen and their Curie temperatures T_M were measured. In each case, the difference in the two T_M values corresponded to composition differences of less than 0·1 at.% Cr. The remainder of the approximately 2 cm long cylindrical ingot was used for the expansion and heat capacity measurements.

To prepare the specimens for measurements of the pressure dependence of T_M, master alloys of compositions 8 at.% Cr and 12·5 at.% Cr were prepared in the same manner as the thermal expansion specimens. Weighed amounts of the master alloys were arc-melted together to obtain approximately 5 g specimens with intermediate compositions. These specimens were heat-treated in the same way as the larger specimens and then spark cut to a toroidal shape.

(*b*) *Apparatus*

Measurements of T_M at zero pressure for the small bars were made using an a.c. susceptibility probe described earlier (Simpson 1979*a*). Absolute errors in these values for T_M are estimated to be less than ± 3 K.

Two coils were wrapped around each toroidal specimen to act as a transformer. This assembly was mounted in a conventional high pressure cell (Itskevich 1964) in which pressures up to 0·6 GPa were generated at room temperature using a 1 : 1 n-pentane, isoamyl alcohol pressure medium and then cooled to the vicinity of T_M. The signal from the secondary coil was plotted on an X–Y recorder, the X-axis of which was driven from a thermometer. Measurements were made while heating and while cooling. The temperature was changed at rates between 4 and 20 mK min^{-1}. Temperature T_M was taken to be the average at which the signal from the secondary coil was greatest. Thermal hysteresis was usually less than 40 mK.

Temperatures above 20 K were measured with a Rosemount E2050 platinum resistance thermometer with relative and absolute accuracies of ± 20 and ± 150 mK respectively. Temperatures below 20 K were measured with a Cryocal CR1000 germanium resistance thermometer calibrated to an absolute accuracy of better than ± 15 mK.

Pressures were measured using superconducting Sn (Smith *et al.* 1969) and Pb (Clark and Smith 1978) manometers to an accuracy of $\pm 0{\cdot}03$ GPa.

We also measured the pressure dependence of the susceptibility of a paramagnetic Ni 12 at.% Cr specimen. After two coils were wrapped around the specimen, it was placed in the high pressure cell and cooled to 4·2 K; the mutual inductance of the coils was then measured using a modified SHE model RBU bridge while cooling to 2 K.

Thermal expansion measurements were made in a three-terminal capacitance dilatometer of similar design to the one described by White and Collins (1972). Above

4·2 K measurements were made according to the procedure followed by White and Collins. Below 4·2 K, the main helium bath was pumped below the λ-point and the temperature of the cell was varied by an electronically controlled heater. The absolute accuracy of the measurements presented here is estimated to be $\pm 6\%$ of the total expansion, subject to a resolution limit of $\pm 1 \times 10^{-9}$ K^{-1}. The experimental method for these measurements has been described in more detail elsewhere (Simpson 1979*b*).

The heat capacity of the alloys was measured in an adiabatic calorimeter (Smith *et al.* 1980) in the temperature range 5–120 K. Typically, the background correction for the sample holder and addenda ranged from 20% to 30% of the total measured heat capacity over the full temperature range. Measurements made on a test sample of pure annealed copper indicated absolute uncertainties of $\pm 3\%$ below 30 K and $\pm 2\%$ above 30 K when compared with standard values (Touloukian and Bayco 1970). The relative uncertainty and reproducibility within a run, as judged from the scatter in the data, is about $\pm 2\%$ below 10 K and about $\pm 1\%$ at 100 K.

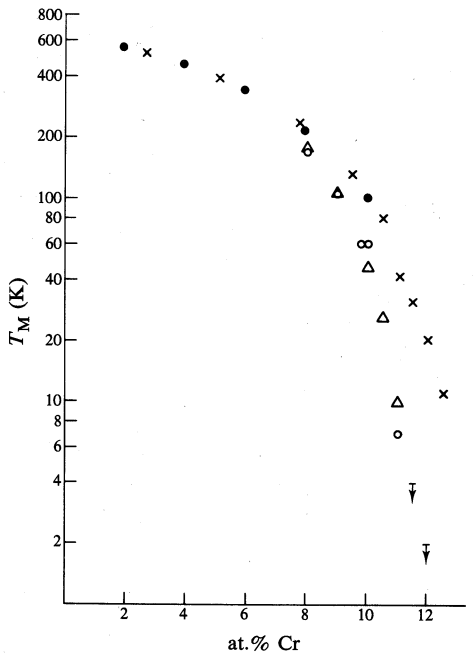

Fig. 1. Magnetic ordering temperature T_M as a function of composition for Ni–Cr solid solution alloys: open circles, small bars cut from large thermal expansion/heat capacity samples; triangles, toroidal pressure measurement samples; crosses, from Besnus *et al.* (1972); solid circles, from Tange *et al.* (1981).

3. Results

(*a*) *Ferromagnetic Ordering Temperature*

The values for the magnetic ordering temperature determined for the small bars cut from the large ingots and for the toroidal high pressure samples are shown in Fig. 1. The detailed shape of the low field a.c. susceptibility in the vicinity of a ferromagnetic transition is a complex function of magnetic domain and demagnetization effects related to the shape of the sample. Consequently, the assignment of a value to the ferromagnetic ordering temperature can be rather arbitrary (Maartense and Williams 1976; Ododo 1979). Maartense and Williams have argued that the most reliable choice of ordering temperature is given by the inflection point in the increase of

susceptibility with decrease of temperature. However, from our measurements on the toroidal specimens we find that the demagnetization effects can significantly influence the temperature at which the inflection point occurs.

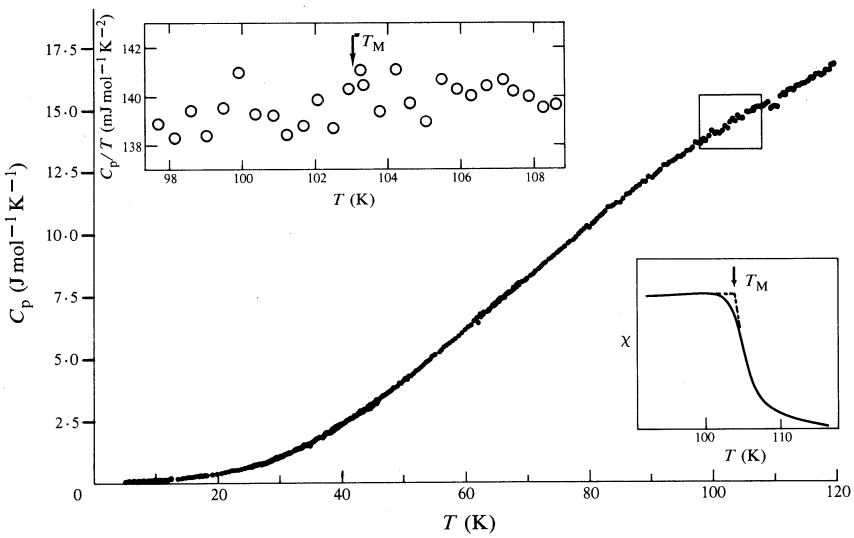

Fig. 2. Specific heat capacity for Ni 9 at.% Cr as a function of temperature. *Upper insert*: C_p/T as a function of temperature on an expanded scale for the indicated region about T_M. *Lower insert*: low field a.c. susceptibility χ; the dashed lines illustrate the construction used to define T_M (see Section 3*a*).

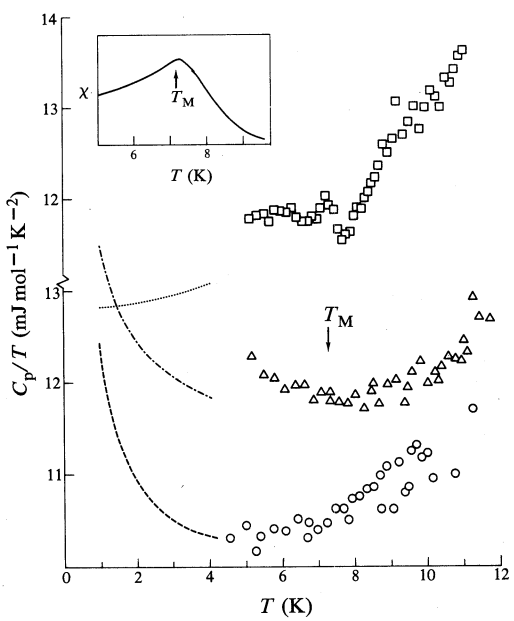

Fig. 3. Low temperature specific heat capacity for Ni–Cr alloys: squares, 9 at.% Cr; triangles, 11 at.% Cr; circles, 12 at.% Cr.

Data of Moody *et al.* (1970) are: dotted curve, 9 at.% Cr; dot–dash curve, 11 at.% Cr; dashed curve, 12 at.% Cr.

Note the displaced vertical scale for the 9 at.% Cr data.

Insert: low field a.c. susceptibility for Ni 11 at.% Cr.

The effects of demagnetization were particularly severe for the small bars cut from specimens containing less than 10 at.% Cr. Demagnetization effects produced a step-like shape for the susceptibility as a function of temperature (see the insert to Fig. 2). The construction used to define the ordering temperature in this case is indicated. For the 11 at.% Cr alloy there was a well defined peak in the susceptibility which we have taken to define T_M (insert Fig. 3). The values of T_M obtained in this manner for the small bars agree well with those derived from the pronounced peaks in the susceptibility measurements for the toroidal specimens for which the demagnetization effects do not occur. The small differences which are found between the two sets of values are consistent with slight differences in composition and are not considered to be significant.

Values for T_M reported by Besnus *et al.* (1972) and Tange *et al.* (1981) are also shown in Fig. 1. These values, which are consistent within themselves, are significantly higher than those for the same compositions presented here. As already noted, this difference may be partly due to the difference in specimen preparation. Furthermore, both previous investigations used extrapolations of high field magnetization data to obtain T_M.

(*b*) *Specific Heat Capacity*

Fig. 2 shows the specific heat capacity of the 9 at.% Cr alloy over the entire range 5–120 K. No unusual behaviour of any kind is evident. The specific heat capacity of this alloy on an expanded scale near T_M is shown in an insert to Fig. 2. Again, there is no evidence for any anomaly.

Fig. 3 shows specific heat capacity measurements at low temperature for the Ni 9, 11 and 12 at.% Cr alloys. Unfortunately, our calorimeter is restricted to temperatures above 4·2 K and consequently the data do not extend down into the temperature range in which the magnetic contribution can be clearly resolved. However, our measurements may be compared with those reported by Moody *et al.* (1970). Our measurements for the 12 at.% Cr alloy fit on well to those of Moody *et al.*, but our measurements for the other two alloys are about 5% higher than the extrapolated data of Moody *et al.* In view of the relatively large absolute uncertainty in our measurements and the possibility of differences between the heat capacities of specimens introduced by different specimen preparation procedures, we do not attach any physical significance to this difference.

There is no anomaly visible in the specific heat capacity of the 11 at.% Cr alloy near T_M, but C_p/T does rise continuously at temperatures below 7 K. There is also evidence of a minimum C_p/T for the 12 at.% Cr specimen at a lower temperature.

For the 9 at.% Cr alloy, T_M for both of the pieces cut from each end was 103 ± 3 K and for the 11 at.% Cr the corresponding values were $6{\cdot}9 \pm 0{\cdot}3$ K and $7{\cdot}2 \pm 0{\cdot}3$ K. An independent measurement made on the entire heat capacity/thermal expansion sample in the thermal expansion cell by winding a coil around the centre of the sample gave $T_M = 6{\cdot}8 \pm 0{\cdot}1$ K. From these measurements of T_M we expect that any heat capacity anomaly at T_M would be broadened by composition inhomogeneity over less than 3 K for the 9 at.% Cr alloy and less than 0·4 K for the 11 at.% Cr alloy.

(*c*) *Thermal Expansion*

The thermal expansion data plotted in the form of α/T as a function of T^2 are shown in Fig. 4. A striking difference in the expansion behaviour for the para-

magnetic (solid symbols) and ferromagnetic (open symbols) alloys is immediately evident. The paramagnetic alloys exhibit an increase in α/T similar in character to the increase in C_p/T which is found for *both* paramagnetic and ferromagnetic alloys about the critical composition, whereas for the ferromagnetic alloys α/T *decreases*. Thus, it is immediately evident that the magnetic contribution to the thermal expansion changes *sign* on passing from the paramagnetic to ferromagnetic state. Furthermore, the magnetic contribution to the thermal expansion is largest for compositions close to the critical composition.

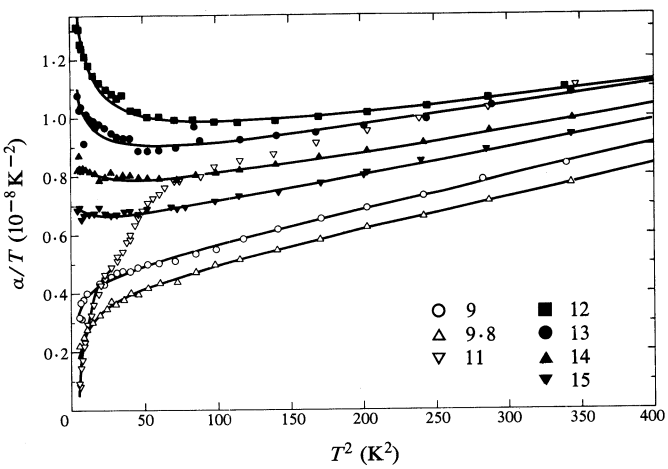

Fig. 4. Thermal expansion in the form of α/T as a function of T^2 for Ni–Cr solid solution alloys. The solid symbols are for paramagnetic alloys, the open for ferromagnetic, with the compositions indicated (in at.% Cr).

Larger scale plots of both the expansion and specific heat capacity data for the 11 at.% Cr alloy in the vicinity of the ferromagnetic ordering temperature are presented in Fig. 5. In contrast to the specific heat capacity data, the thermal expansion data have evidence of a slight 'kink' at T_M. Assigning a value of -1×10^{-9} K^{-2} to the discontinuity in α/T and using $dT_M/dP = -0{\cdot}72$ K GPa^{-1} (see Section 3*f* below) in the Ehrenfest equation gives a value of $0{\cdot}2$ mJ mol^{-1} K^{-2} for the discontinuity in C_p/T which would be too small to be resolved in the specific heat capacity data.

(*d*) *Thermodynamic Data Analysis*

In an effort to identify the individual contributions to the heat capacity and thermal expansion the data have been least-squares fitted to an expansion of the form (1). The temperature ranges of the fits were limited to $T < 15$ K for the specific heat capacity and $T < 20$ K for the thermal expansion. In the case of the thermal expansion data for the 11 at.% Cr sample the data below 5 K were fitted to the expression $(\alpha - cT^3)/T = a/T + b$, where c was taken to be $0{\cdot}74\times10^{-11}$ K^{-4}, to avoid the discontinuity in the temperature dependence of the expansion coefficient at the magnetic ordering temperature. The two sets of coefficients A, B, C for the specific heat capacity and a, b, c for the thermal expansion are plotted as a function of composition in Fig. 6. The fits for the specific heat capacity data can only be expected to give relatively crude estimates of the coefficients B and C due to the lack

of data below 4·5 K (the contribution from A being negligible above 4·5 K). Nevertheless, these coefficients agree quite well with those obtained by Moody *et al.* (1970), which are plotted in Fig. 6*a*.

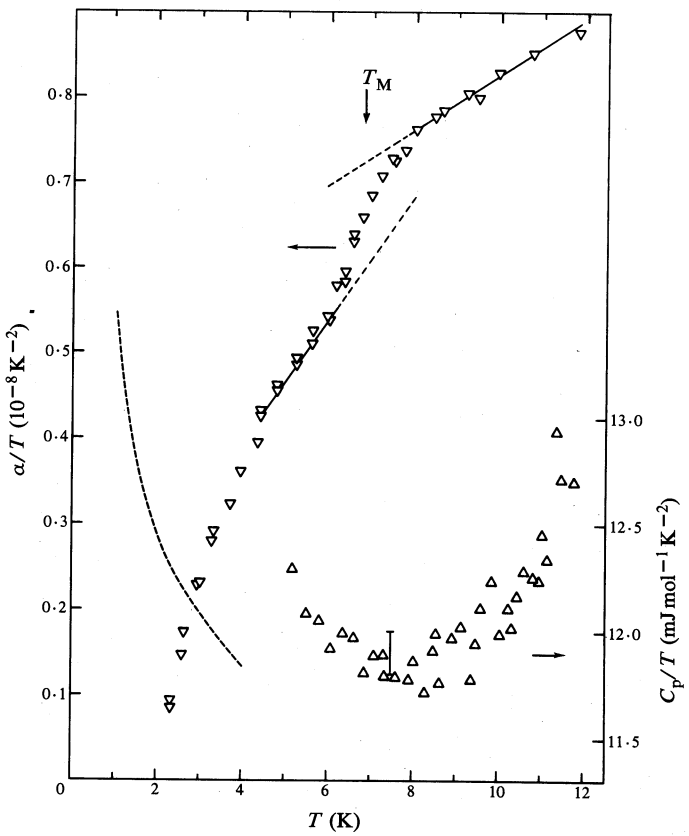

Fig. 5. Low temperature specific heat capacity and thermal expansion data for Ni 11 at.% Cr. The dashed curve on the left represents the data of Moody *et al.* (1970). The bar shown in the specific heat capacity data represents the magnitude of the discontinuity calculated from the discontinuity in α/T using the Ehrenfest equation.

The fits to the expansion data are indicated by the lines drawn in Fig. 4. While these lines fit the data to within $\pm 2\%$, it is impossible to judge to what extent the three coefficients represent an accurate separation of the magnetic, electronic and lattice components. It is suspected that there may be a significant magnetic contribution to the linear T term and such a departure from the approximation of a constant term would also influence the T^3 coefficient (Hahn and Wohlfarth 1968). This is illustrated by the negative and near zero values for the T^3 coefficient that Moody *et al.* (1970) found from the least-squares fitting of their heat capacity data. Similar effects can be expected for the fitting of the expansion data.

In spite of the reservations, it is quite clear that the sign of the magnetic contribution to the thermal expansion changes on passing from the ferromagnetic to the paramagnetic state. Coupled with this, there appear to be broad maxima in the

electronic contributions to both the heat capacity and the thermal expansion. The concentration dependence for the lattice term is far more uncertain, but from a consideration of the Grüneisen parameter, discussed below, it seems likely that the phonon contribution to both the heat capacity and the thermal expansion decreases smoothly with increasing Cr content.

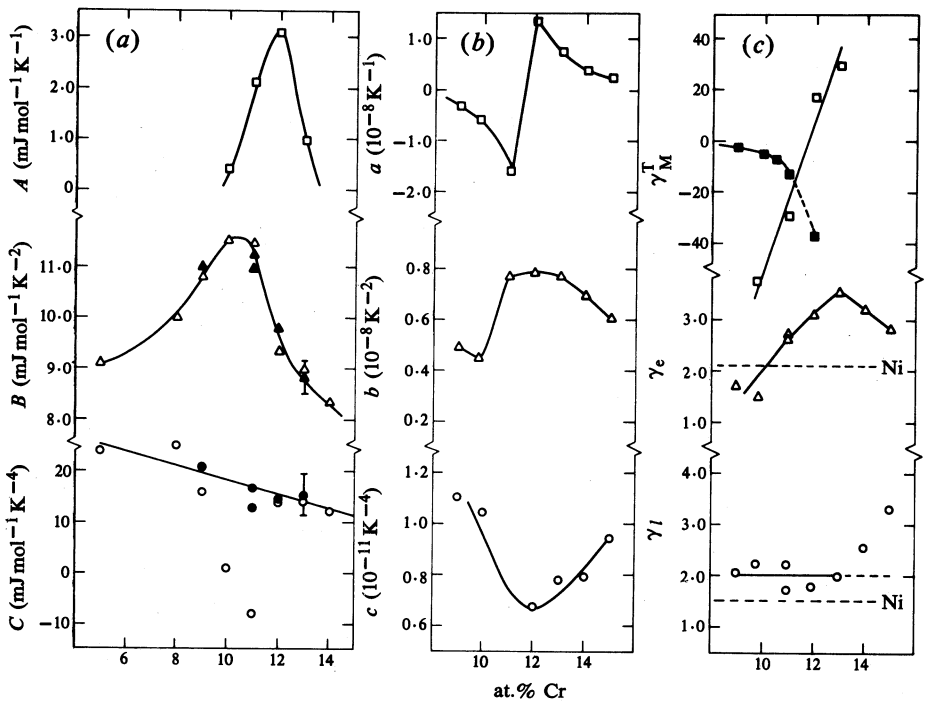

Fig. 6. Least-squares fitting coefficients for (*a*) the specific heat capacity, (*b*) the thermal expansion, and (*c*) the magnetic, electronic and lattice Grüneisen parameters calculated from them as a function of Cr concentration. Note the data for the 12 at.% Cr alloy were taken in the paramagnetic state. The open symbols in (*a*) are taken from Moody *et al.* (1970). The solid symbols in (*c*) represent values of γ_M derived from measurements of dT_M/dP. Dashed lines are for pure Ni (White 1965).

(*e*) *Thermodynamic Grüneisen Parameters*

The individual Grüneisen parameters calculated from the appropriate heat capacity and thermal expansion coefficients using expression (2) are shown in Fig. 6*c*. The bulk modulus of Ni of 190 GPa was used in the calculations for all compositions.

The extent to which the apparent composition dependence of the Grüneisen parameters γ_e and γ_l, which are identified with the electronic and lattice excitations respectively, is real is debatable since neither the volume dependence of the lattice nor the electronic excitations are expected to be very sensitive to composition. It is probable that the variations stem, at least in part, from the inadequate separation of the three contributions. It may be noted that only relatively small adjustments would be required to the composition dependences of B and b for γ_l to become constant at a value of about 2. The electronic and lattice Grüneisen parameters for pure Ni (White 1965) are also included in Fig. 6*c* (dashed lines).

(*f*) *Pressure Dependence of* T_M

The ferromagnetic ordering temperature decreased linearly with pressure between 0 and 0·6 GPa for the alloys with compositions between 9 and 11 at.% Cr. Values of dT_M/dP were computed from lines of best fit to the data and these are plotted as a function of T_M in Fig. 7. Fig. 7 also includes the value of dT_M/dP (solid triangle) obtained for an Ni 11·5 at.% Cr specimen which had been quenched from 900°C into water. This quenching had raised T_M from below 4 K to 11·4 K, close to the T_M for the 11 at.% Cr specimen. The value of dT_M/dP for the quenched specimen is also close to that for the 11 at.% Cr specimen (i.e. $-0{\cdot}72$ K GPa^{-1}; see Section 3*c*), which suggests that T_M rather than the chemical composition determines the magnitude of dT_M/dP in Ni–Cr alloys.

In order to analyse the susceptibility measurements made under pressure on the paramagnetic 12 at.% Cr specimen, the output from the secondary coil was least-squares fitted to an offset Curie–Weiss law of the form

$$M = X + Y/(T - T_M).$$

This expression fits the data to within $\pm 0{\cdot}02\%$ and gives a zero pressure value for T_M of $0{\cdot}59 \pm 0{\cdot}01$ K and $dT_M/dP = -0{\cdot}11 \pm 0{\cdot}06$ K GPa^{-1}.

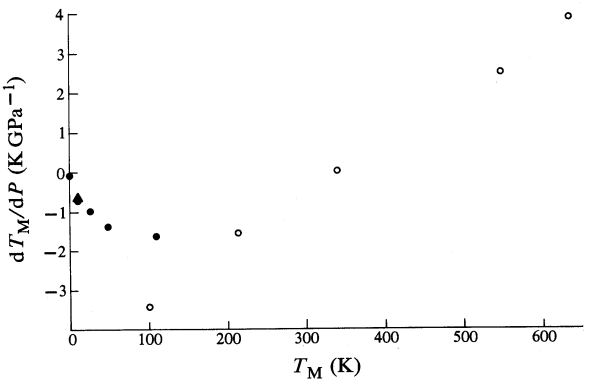

Fig. 7. Values of dT_M/dP as a function of T_M for Ni–Cr solid solution alloys (solid symbols). The open symbols are taken from Tange *et al.* (1981).

Fig. 7 also includes values for dT_M/dP reported by Tange *et al.* (1981). It should be recalled that these authors prepared their samples by water quenching and obtained higher values of T_M as a function of composition than for the alloys studied here (see Fig. 1). However, in view of the apparent correlation between T_M and dT_M/dP noted above, we do not regard this to be a serious obstacle to the combination of the two sets of data. It is seen from the combined data that dT_M/dP initially decreases with the addition of Cr (decreasing T_M), changing from positive to negative in sign for T_M close to 350 K. This trend reverses for $T_M < 100$ K and $dT_M/dP \to 0$ as $T_M \to 0$. Similar behaviour has been observed in other Ni based solid solution alloys (Kadomatsu and Fujiwara 1979).

From our values of dT_M/dP we have calculated $-d\ln T_M/d\ln V$ using the bulk modulus for Ni, and these values for γ_M are plotted in Fig. 6*c*. While the values of γ_M and γ_M^T are of the same sign for the ferromagnetic alloys, there is a striking difference in their magnitudes and composition dependences.

4. Discussion

There are three significant features in the data presented:

(1) the absence of any anomaly in the heat capacity at T_M;
(2) the difference in the magnitudes of γ_M and γ_M^T;
(3) the change in sign of γ_M^T in passing from the ferromagnetic to paramagnetic regime.

The molecular field model predicts a discontinuity in the heat capacity at T_M of $1{\cdot}5Nk$ for an array of N spins with $S = \frac{1}{2}$ (Smart 1966). This value is appropriate to a uniform distribution of magnetic moment, whereas it has been long established from neutron scattering studies (Low 1969) that the distribution of magnetic moments is highly inhomogeneous in the vicinity of the critical composition for ferromagnetic ordering. In the case of Ni–Cr alloys, the number of magnetic clusters is estimated to be approximately 1% and 0·5% of the total number of atoms for 9 and 11 at.% Cr respectively (Rainford *et al.* 1971). Thus, the values for the anticipated discontinuity in C_p/T_M are reduced to approximately 1·3 and 8 mJ mol^{-1} K^{-2} respectively. In the case of the 9 at.% alloy, a discontinuity of this magnitude could easily be masked by the scatter in the data. However, that for the 11 at.% alloy should have been clearly visible.

The absence of an anomaly at T_M in the heat capacity of Ni–Cu alloys close to the critical concentration has also been noted (Aitken *et al.* 1981; Chen and Loram 1981), although a sharp cusp in C_p/T was observed for alloys containing more than 50 at.% Ni (Chen and Loram 1981). However, the magnitudes of these cusps were such that they would not have been resolved in our measurements. Chen and Loram have argued in favour of the spin-fluctuation model, whereas Aitken *et al.* have interpreted their data, which were in zero and applied magnetic fields, in terms of the spin glass freezing of magnetic clusters. The absence of a heat capacity anomaly at the spin glass ordering temperatures is well known, but in the present case both the sign of γ_M and the discrepancy between it and γ_M^T lead us to believe that the magnetic behaviour is not spin glass in character. Specifically, for spin glass alloys γ_M is positive and good agreement is observed between γ_M and γ_M^T (Simpson *et al.* 1981; Smith 1981).

The observation (1) may equally well be taken to indicate that either only a small fraction of the magnetic clusters are involved in the ordering at T_M, or the number of degrees of freedom of each individual cluster is not significantly affected by the onset of ferromagnetism. In the former case, the majority of the magnetic clusters gradually align as the temperature is reduced below T_M, which produces the low temperature magnetic contribution to the heat capacity. The latter case may be most readily understood by considering two energies characteristic of the cluster and the individual spins. For convenience we shall refer to these as the inter-cluster and intra-cluster energies. These energy terms themselves may have complex compositions with direct and indirect exchange contributions to the inter-cluster energy and exchange and anisotropy contributions to the intra-cluster energy (Soukoulis and Levin 1977).

The latter model has the advantage that it can readily account for the observation (2) if it is assumed that the low temperature magnetic contributions to the thermodynamic properties are dominated by the intra-cluster energy, whereas the volume dependence of the ordering temperature is determined by the inter-cluster energy.

With us having attributed the primary responsibility for the low temperature contributions to the specific heat capacity and the thermal expansion to the intra-cluster energy, the sensitivity of both the sign and the magnitude of γ_M^T to the transition to the magnetically ordered state is surprising and leads us to suggest that the intra-cluster energy represents a delicate balance between terms having comparable, but opposite, volume dependences.

It is interesting to note that Moriya and Usami (1980) predict in the context of the spin-fluctuation model that the magnetic Grüneisen parameter should change sign close to the critical composition. Should this predicted sign change be a consequence of a heterogeneous spin distribution, rather than being inherently linked to the band model, it could equally well be applicable to a cluster model and may provide the explanation of the present observations.

Acknowledgment

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