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1990 J. Phys.: Condens. Matter 2 6251

(http://iopscience.iop.org/0953-8984/2/29/002)

J. Phys.: Condens. Matter 2 (1990) 6251–6262. Printed in the UK

Magnetic Grüneisen parameters in Cr alloys

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Received 1 August 1989, in final form 7 March 1990

Abstract. The Stoner–Wohlfarth (SW) and Grüneisen–Testardi (GT) methods for analysing and parametrising the magnetic contributions to the thermal expansion and the bulk modulus of weak magnetic systems are compared. The GT theory is employed to analyse the magnetoelastic data for Cr alloy spin-density-wave systems, which had previously been treated by use of the SW theory. In Cr–Mo the magnetic Grüneisen parameters, Γ_{SF} in the paramagnetic phase, and Γ_{NT} in the ordered state, decrease monotonically as the Mo concentration increases up to about 10 at.%. In Cr–Al, on the other hand, Γ_{SF}, and Γ_{SW} at zero temperature, show a gigantic peak centred at about the composition, Cr + 2.2 at.% Al, close to the triple point, while Γ_{NT} is roughly constant throughout the singular region. General features of the behaviour of the magnetic Grüneisen parameters, as functions of solute concentration in Cr alloy systems, and in pure Cr, are discussed.

1. Introduction

The spin-density wave (SDW) in chromium (Fawcett 1988) and its dilute antiferromagnetic alloys (Alberts 1989a) gives rise to large magnetic contributions to the thermal expansion and elastic constants, which are indicative of strong magnetoelastic coupling. The analysis of these magnetic contributions is considerably simplified in the case of pure Cr (Muir et al. 1987a, Fawcett 1989a), and we can assume the same is true for the dilute antiferromagnetic alloys, by the fact that the strain dependence of the magnetic properties is largely a volume dependence, since the magnetoelastic tensor of Cr is almost isotropic and the off-diagonal shear components are small (Muir *et al* 1987b); and futhermore that the strain dependences are essentially linear.

Two different phenomenological theories have been used to analyse, and thus parametrise, the magnetic contributions to the volume thermal expansivity $\Delta\beta$ (or equivalently the magnetovolume $\Delta\omega$) and the bulk modulus ΔB of the SDW in Cr and its dilute alloys. Alberts (1989a) applies to these antiferromagnetic metals the expressions for $\Delta\beta$ and ΔB which Steinemann (1978) derived from the Stoner–Wohlfarth (SW) theory for weak itinerant ferromagnets. In this mean-field SW theory, the magnetic free energy ΔF has an explicit temperature dependence, and its volume dependence is introduced through a volume-dependent Néel temperature, $T_N(\omega)$, ω being the volume strain.

On the other hand, Fawcett (1989a) follows Testardi (1975), and considers ΔF to be a general function of reduced temperature, $t = T/T_i(\omega)$, where $T_i(\omega)$ is a different

0953-8984/90/296251+12$03.50

volume-dependent characteristic temperature in each temperature regime. In particular, $T_{SF}(\omega)$ is the spin-fluctuation-temperature function corresponding to the paramagnetic phase, while $T_{NT}(\omega)$ is the Néel-temperature function corresponding to the ordered phase. This Grüneisen–Testardi (GT) theory, as employed by Fawcett(1989a), expresses the volume dependence of the magnetic properties in terms of several magnetic Grüneisen parameters, $\Gamma_i = -\mathrm{d}(\ln T_i(\omega))/\mathrm{d}\omega$.

We note that both the SW theory (Steinemann 1978) and the GT theory (Testardi 1975) were developed for application to ferromagnetic systems. For an incommensurate antiferromagnet, in mean-field theory, the energy will be a function of the square of the amplitude of the SDW, which corresponds to the square of the magnetisation in a ferromagnet. Thus either theory should apply equally well to a SDW system or to a ferromagnet.

In this paper, we apply the GT theory to the analysis and parametrisation of the magnetoelastic data for the Cr alloy systems, Cr–Mo and Cr–Al. In section 2 we outline the two theories and quote the expressions used to analyse the magnetoelastic data. In section 3 we use the expressions corresponding to the GT theory to obtain magnetic Grüneisen parameters from the data of Alberts (1989a) and his co-workers, who in their publications have employed the SW theory. We discuss in section 4 the extent to which the GT theory is successful in parametrising the observed magnetoelastic behaviour of several Cr alloy systems, general features of the concentration dependence of the magnetic Grüneisen parameters, and especially interesting features for particular systems.

2. Theory

In the SW theory (Steinemann 1978), one writes

$$\Delta F(t) = \varphi(1-t)^2 \qquad t(\omega) = T/T_N(\omega) \qquad \varphi = a[T_N(\omega)]^4 . \tag{1}$$

Thus the prefactor φ depends on volume through the volume-dependent Néel-temperature function $T_N(\omega)$ whose single-letter subscript distinguishes it from the equivalent Néel-temperature function $T_{NT}(\omega)$ of the GT theory. Equation (1) gives a magnetovolume

$$\Delta\omega(t) = -(4\varphi/B)\Gamma_{SW}(1-t^2) \tag{2}$$

with

$$\Gamma_{SW} = -\mathrm{d}\ln T_N(\omega)/\mathrm{d}\omega . \tag{3}$$

Γ_{SW} may be termed the SW Grüneisen parameter corresponding to the SW magnetic free energy (1).

The magnetic contribution to the bulk modulus obtained from (1) is (Alberts and Lourens 1984)

$$\Delta B(t) = -4\varphi\Gamma_{SW}^2(3-t^2) . \tag{4}$$

We note that the SW theory gives a magnetic contribution at zero temperature to both the magnetovolume and the bulk modulus, respectively

$$\Delta\omega(0) = -(4\varphi/B)\Gamma_{SW} \tag{5}$$

and

$$\Delta B(0) = -12\varphi\Gamma_{SW}^2 . \tag{6}$$

Comparison of these two results provides therefore a measure of the SW zero-temperature Grüneisen parameter

$$\Gamma_{SW} = \frac{1}{3B}\frac{\Delta B(0)}{\Delta\omega(0)}. \tag{7}$$

In the GT theory (Fawcett 1989a), the magnetic free energy is written, in the ordered state below the Néel temperature T_N

$$\Delta F(t) = f[t_{NT}(\omega)] \qquad t_{NT}(\omega) = T/T_{NT}(\omega) \qquad T < T_N \tag{8}$$

and in the paramagnetic phase, above T_N

$$\Delta F(t) = g[t_{SF}(\omega)] \qquad t_{SF}(\omega) = T/T_{SF}(\omega) \qquad T > T_N. \tag{9}$$

The Néel-temperature function $T_{NT}(\omega)$ (where the T in the subscript denotes Testardi (1975)) is thus distinguished from the spin-fluctuation-temperature function $T_{SF}(\omega)$, in accordance with the experimental fact that in Cr the two quantities give very different Gruñeisen parameters. The notation $T_{NT}(\omega)$ is used (rather than simply $T_N(\omega)$, as in Fawcett (1989a, 1989b, 1989c and 1989d)), to avoid confusion with the function $T_N(\omega)$, which is employed in the SW theory, as in (1).

It is then argued that, close to the Néel temperature, the second derivative for both $f(t)$ and $g(t)$ will be large compared with the first derivative. In the approximation that the latter can be neglected, two magnetic Gruñeisen parameters are thus obtained

$$\Gamma_{NT} = -\frac{d(\ln T_{NT}(\omega))}{d\omega} = -\frac{1}{B_N T_N}\lim_{t\leq 1}\left(\frac{\Delta B(t)}{\Delta\beta(t)}\right) \tag{10}$$

and

$$\Gamma_{SF} = -\frac{d(\ln T_{SF}(\omega))}{d\omega} = \lim_{t\geq 1}\left(\frac{\Delta B(t)}{\Delta\beta(t)}\right)\left(-\frac{1}{B_N T_N}\right) \tag{11}$$

where B_N is the bulk modulus at T_N. We have again changed the notation in the interest of clarity. Fawcett (1989a) distinguishes by superscripts the Grüneisen parameters Γ^I and Γ^{II} obtained by comparing, respectively, ΔC with $\Delta\beta$ and $\Delta\beta$ with ΔB, where ΔC is the magnetic contribution to the specific heat. Thus we have the equivalence between the two notations, $\Gamma_{NT} \equiv \Gamma^{II}_{-}$, and $\Gamma_{SF} = \Gamma^{II}_{+}$. We adopt this new notation since in Cr and Cr alloys the large values of the magnetic Grüneisen parameters, and the relatively high Néel temperature, result in ΔC being only a small fraction of C. Thus in pure Cr, just below the Néel temperature, we find that $\Delta C/C \simeq 0.1\%$ (Williams *et al* 1979), and accordingly the accuracy with which one can determine the corresponding Grüneisen parameter, $\Gamma^I_{-} = -75 \pm 25$, is poor (Fawcett *et al* 1986a). To our knowledge there are no data for the specific heat of Cr alloys accurate enough to determine Γ^I, so that the superscript notation is superfluous.

In practice, the requirement that Γ_{NT} and Γ_{SF} in (10) and (11) should be determined only in the limit of temperature approaching T_N from below and above, respectively, is not stringent. In Cr, for example, the magnetic contributions, $\Delta\beta(t)$ and $\Delta B(t)$, with reduced temperature t as the variable parameter, give a linear plot over a temperature range of at least 100 K, both above and below the Néel temperature, $T_N \simeq 311$ K, but with different slopes corresponding to the different values of Γ_{NT} and Γ_{SF} (Muir *et al* 1987a). In the Cr alloys that we have analysed, the linear

region does not extend all the way to the Néel temperature T_N, either from above T_N in the paramagnetic phase, i.e., for $t = T/T_N > 1$, or from below T_N in the ordered state, i.e., for $t < 1$. The range of values of t for the linear portion of the plot of $\Delta B(t)$ vs. $\Delta\beta(t)$ varies considerably, as we shall see in section 3. When in practice we apply (10) and (11) to determine the magnetic Grüneisen parameters Γ_{NT} and Γ_{SF}, we take the slope of the linear portion of the appropriate plot, and *not* the limit, $t \to 1$.

The other difficulty in applying (10) and (11) to the analysis of magnetoelastic data is the choice of B_N, on the one hand because of the rapid variation with temperature of the bulk modulus around the Néel transition, and on the other because its value for the reference material may be considerably different from that of the alloy under study. The values of B_{N-} and B_{N+} used for B_N in (10) and (11), respectively, are rough averages between those of the alloy and of Cr + 5 at.% V over the temperature regions of interest.

The fact that Γ_{SF}, in particular, is not determined in the limit, $t \to 1$, as implied by (11), but instead is obtained from the temperature dependence over some temperature region, $t > 1$, that in nearly all cases does not extend as far as $t = 1$, means that this magnetic Grüneisen parameter is not characteristic of critical fluctuations. The experimental work analysed here did not attempt the difficult task of measuring $\beta(t)$ and $B(t)$ with high resolution in temperature right up to the Néel transition (which would ideally have to be a continuous transition) so as to determine Γ_{CF}, the magnetic Grüneisen parameter characteristic of critical fluctuations.

In the low temperature region, the GT theory, as developed by Fawcett (1989a), employs two strain-dependent parameters to describe the magnetic free energy. We shall be concerned in the Cr alloys, however, only with the magnetic Grüneisen parameter defined by the ratio of the zero-temperature magnetic contributions to the bulk modulus and magnetovolume

$$\Gamma_{GT} = \frac{1}{B}\frac{\Delta B(0)}{\Delta\omega(0)} \tag{12}$$

Again we have changed the notation, since Fawcett (1989a) writes $\Gamma_{GT} \equiv \Gamma_0^{III}$. We do so in order to emphasise the difference, by a factor three, in the definition through (12) of the magnetic Grüneisen parameter Γ_{GT} at zero temperature in the GT theory, and Γ_{SW} defined through (7) in the SW theory. We note also that in both equations the bulk modulus B in the denominator, which was denoted B_0 by Fawcett (1989a), in practice is taken to be the average between that of the reference material and the sample.

We note finally in this section that a magnetic Grüneisen parameter may be defined from the discontinuities in the volume thermal expansivity $\Delta\beta_N$ and the bulk modulus ΔB_N at the Néel temperature, by use of the Ehrenfest relation

$$\Gamma_E = -\frac{1}{B_N T_N}\frac{\Delta B_N}{\Delta\beta_N} \tag{13}$$

This mean-field expression should be applied strictly only to a second-order transition, but the first-order transition in Cr is so weak that (13) is probably a good approximation (Walker 1980).

There are severe practical difficulties however in applying (13) to the analysis of Cr data, since it is not feasible to determine $\Delta\beta_N$ and ΔB_N from even the highest quality experimental results (Fawcett *et al* 1986b and Muir *et al* 1987b, respectively). This is

why Muir *et al* (1987a) adopted the much more accurate procedure of determining magnetic Grüneisen parameters in the limit, $t \rightarrow 1$, as expressed in (10) and (11). They found furthermore quite different values for Γ_{NT} and Γ_{SF}, so that, even if it were possible to estimate Γ_E from the Cr data, it would be difficult to assess its significance. We shall see in section 4, however, that Γ_E agrees well with Γ_N in the Cr–Al system, and provides a useful complement to the direct pressure measurements.

3. Analysis of experimental data

We analyse first the experimental data for Cr–Mo alloys. Venter *et al* (1986) measured, over the temperature range 77–400 K, the thermal expansivity $\Delta\beta$ relative to that of the paramagnetic alloy, Cr + 5 at.% V, and the bulk modulus B for six Cr–Mo alloys of composition in the range Cr + 2.82 at.% Mo to 17.40 at.% Mo. They determined the magnetic contribution ΔB to the bulk modulus by subtracting from the value of B that for Cr = 5 at.% V (Alberts and Lourens 1985) at the corresponding temperature.

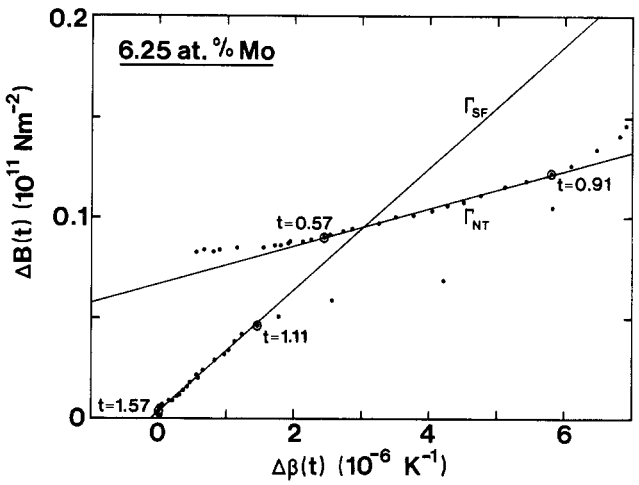

Figure 1. Comparison of the magnetic contributions to the bulk modulus $\Delta B(t)$ and volume thermal expansivity $\Delta\beta(t)$ in Cr + 6.25 at.% Mo. The reduced temperature, $t = T/T_N$, is relative to the Néel temperature, T_N = 230 K. The lines are least-squares fits to the data points between and including the circled points, for which values of t are shown. The slopes when substituted in (10) and (11): for temperature, $T < T_N$, with $B_{N-} = 1.96 \times 10^{11}$ N m^{-2}, $\Gamma_{NT} = -21.0 \pm 0.3$; for $T > T_N$, with $B_{N+} = 2.02 \times 10^{11}$ N m^{-2}, $\Gamma_{SF} = -65 \pm 1$ (data from Venter *et al* (1986)).

We have used these data to determine the magnetic Grüneisen parameters of Cr–Mo alloys from the linear portions of the plots of ΔB versus $\Delta\beta$, both above and below the Néel transition. A representative plot for Cr + 6.25 at.% Mo is shown in figure 1. Normally each plot is linear over a wide temperature range, as in the case of pure Cr (Muir et al. 1987), but with a deviation from linearity in all cases as temperature T approaches the Néel temperature T_N from below, $T < T_N$, as in figure 1, typically at a value of the reduced temperature, $t \simeq 0.90$. For $T > T_N$, the plot is typically linear down to a value, $t \simeq 1.05$, closer to the Néel temperature. The data for the samples richer in Mo, Cr + 13.93 at.% Mo and 17.40 at.% Mo, did not

give satisfactory plots and are not used. The magnetic Grüneisen parameters, Γ_{NT} and Γ_{SF}, are obtained from the slopes of the linear portions of these plots, by the use of (10) and (11). The standard deviation of each value is calculated from the deviation of the points included in the linear plot, and does not include an estimate of the probable error in the average value of B used in place of B_N in (10) and (11). Any such error would apply roughly systematically to all the alloys.

The magnetic Grüneisen parameter Γ_{GT} is obtained from the extrapolations to zero temperature of the magnetovolume $\Delta\omega(0)$ and bulk modulus $\Delta B(0)$, given in figures 4 and 5 respectively, of Venter *et al* (1986). These are substituted in (12), with the bulk modulus taken to be the average value at zero temperature for the alloy and for Cr + 5 at.% V.

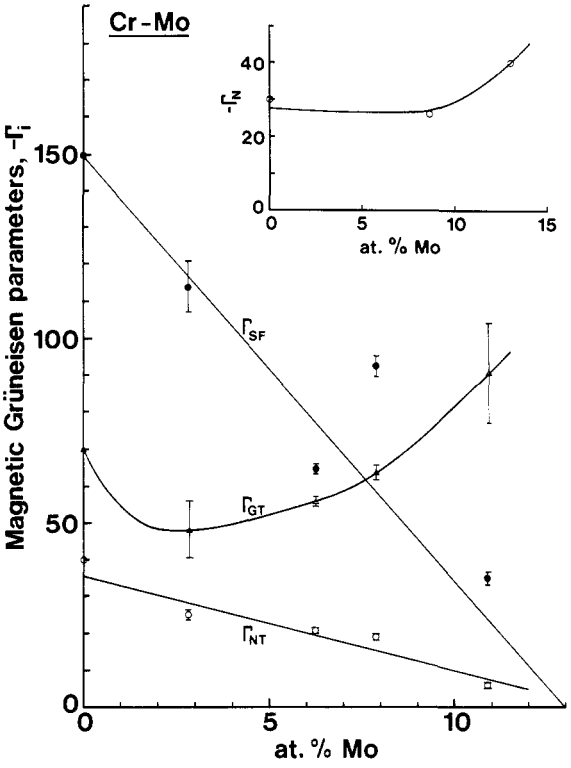

Figure 2. Magnetic Grüneisen parameters Γ_i in Cr–Mo alloys: ●, Γ_{SF} for $T > T_N$; ○, Γ_{NT} for $T < T_N$; △, Γ_{GT} ($3\Gamma_{SW}$) for zero temperature. Inset: ○, Γ_N for $T = T_N$ (data from Rice *et al* (1969)).

The magnetic Grüneisen parameters are shown as functions of Mo concentration in figure 2. Both Γ_{SF} and Γ_{NT} fall monotonically with increasing Mo concentration, as shown by the straight lines, which are guides to the eye. The zero-temperature parameter Γ_{GT} falls initially, but then increases at the higher concentrations. The magnetic Grüneisen parameter Γ_N, obtained from the pressure dependence of the Néel temperature, appears to behave like Γ_{GT}.

We turn now to the analysis of the experimental data for the Cr–Al system. Alberts and Lourens (1984) measured six samples having compositions in the range, Cr + 0.67 at.% Al to 3.22 at.% Al. Data for a representative sample, Cr + 1.7 at.% Al

are shown in figure 3. In the case of Cr–Al, the linear portion of the plot of ΔB versus $\Delta\beta$ comes quite close to T_N, for low concentrations of Al. However, as one approaches the singular region, which extends over concentrations from about 1.8 to 2.6 at.% Al, as shown in figure 4, the deviation from linearity moves to lower values of t, e.g., $t = 0.79$, at concentration 1.7 at.% Al, as illustrated in figure 3. As in the case of Cr–Mo, the linear portion of the ΔB versus $\Delta\beta$ plot for $T > T_N$ in Cr–Al normally comes rather closer to $t = 1$ than for $T < T_N$.

A most remarkable feature of the plot of magnetic Grüneisen parameters of Cr–Al alloys as a function of Al concentration, shown in figure 4, is the gigantic peak, centred on the composition of about Cr + 2.2 at.% Al, for both Γ_{GT} and Γ_{SF}. The absence of any such peak for Γ_{NT} is equally remarkable. This magnetic Grüneisen parameter, which is characteristic of the volume and temperature dependence of the magnetoelastic properties in the ordered state, remains essentially constant across the composition range, as shown in the lower panel of figure 4. The peculiar behaviour of the bulk modulus as a function of temperature for the sample of composition, Cr + 2.19 at.% Al, near the centre of the singular region, which is shown in figure 3 of Alberts and Lourens (1985), unfortunately makes it impossible to determine Γ_{NT} for this alloy.

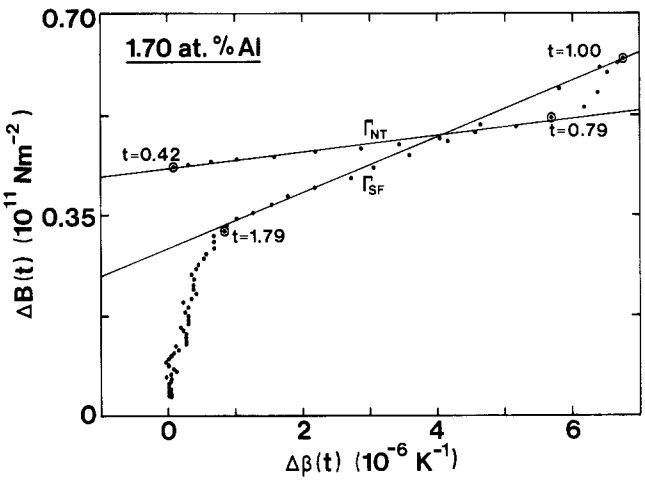

Figure 3. Comparison of the magnetic contributions to the bulk modulus $\Delta B(t)$ and volume thermal expansivity $\Delta\beta(t)$ in Cr + 1.70 at.% Al. The reduced temperature, $t = T/T_N$, is relative to the Néel temperature $T_N = 95$ K. The lines are least-squares fits to the data points between and including the circled points, for which values of t are shown. The slopes give, when substituted in (10) and (11): for temperatures, $T < T_N$, with $B_{N-} = 1.7 \times 10^{11}$ N m^{-2}, $\Gamma_{NT} = -88 \pm 4$; for temperatures, $T > T_N$, with $B_{N+} = 1.8 \times 10^{11}$ N m^{-2}, $\Gamma_{SF} = -286 \pm 18$; (data after Alberts and Lourens (1984)).

The pressure dependence of the Néel temperature was measured by Alberts and Burger (1978) only up to a concentration of 1.99 at.% Al, since alloys having concentrations of 2.3 and 3.4 at.% Al showed no resistance anomaly at the Néel transition. Their results nevertheless show that Γ_N also increases rapidly as the singular region is approached, as illustrated in figure 4.

We note that the pressure dependence of the Néel temperature is so large that,

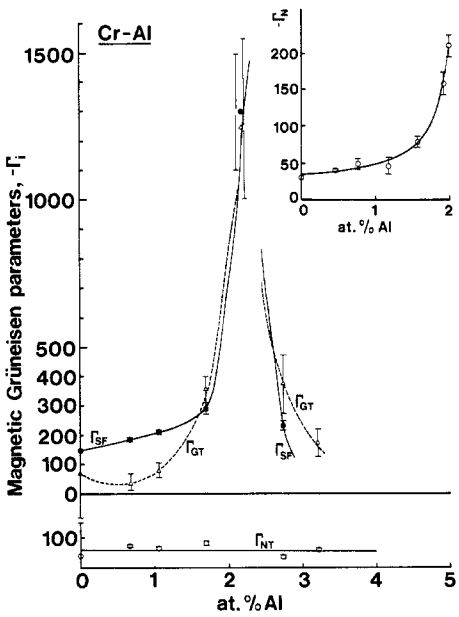

Figure 4. Magnetic Grüneisen parameters Γ_i in Cr–Al alloys: ●, Γ_{SF} for $T > T_N$; ○, Γ_{NT} for $T < T_N$ (lower panel); Δ and – – –, Γ_{GT} ($3\Gamma_{SW}$, for zero temperature). Inset: ○, Γ_N for $T = T_N$ (data after Alberts and Burger (1978)).

when the magnetic Grüneisen parameter is determined, the expression

$$\Gamma_N = -\frac{d(\ln T_N)}{d\omega} = B_N \frac{d(\ln T_N)/dp}{1 - \beta_N B_N (dT_N/dp)} \tag{14}$$

should be used. The correction for finite change in T_N appears in the denominator. It reduces the value of Γ_N by about 50% for the largest value of the pressure dependence, $dT_N/dp = -24$ K kbar^{-1}, for the sample, Cr + 1.99 at.% Al.

4. Discussion

The most important general result of this analysis is that the GT theory appears to describe satisfactorily the relation between the temperature dependence of the magnetic contributions to the thermal expansion and the bulk modulus of Cr alloys, in both the ordered state and in the paramagnetic phase. Just as in pure Cr (Muir *et al* 1987a, Fawcett 1989a), the Grüneisen parameters characteristic of the two temperature regions, Γ_{NT} and Γ_{SF}, are distinctly different.

We might remark in this connection that the magnetic Grüneisen parameter Γ_E, obtained by use of the Ehrenfest relation (13), should be identical to both Γ_{NT} and Γ_{SF}, as defined in (10) and (11). We use these equations differently, however, and determine Γ_{NT} and Γ_{SF}, not in the limit, $t \to 1$, but from the linear portions of the plot of $\Delta B(t)$ versus $\Delta\beta(t)$, for $t < 1$ and $t > 1$, respectively. These linear portions terminate typically at $t \simeq 0.90$ and $t \simeq 1.05$, and the non-linear region closer to $t = 1$ is not capable of analysis, except in some cases for the point, $t = 1$, itself, where both (10) and (11) reduce to (13).

Alberts and Lourens (1984: see their figure 6) found that, in the Cr–Al system, Γ_N and Γ_E follow each other closely in the approach to the peak shown in figure 4, for both higher and lower concentrations of Al. This is to be expected, since (13) is a thermodynamic relation, which must be rigorously satisfied for a second-order transition, and might also be expected to be approximately true for a weak first-order transition. We note in figure 4, however, that Γ_N (and Γ_E from figure 6 of Alberts and Lourens (1984)) is somewhat smaller that Γ_{SF}, though roughly equal to Γ_{GT}, until the latter begins to increase rapidly with increasing Al concentration at the composition of about Cr + 1.7 at.% Al.

The GT theory also describes satisfactorily the behaviour of Cr in the low-temperature regime (Fawcett 1989a), and in the Cr alloys provides a zero-temperature magnetic Grüneisen parameter Γ_{GT}. The SW theory provides a magnetic Grüneisen parameter here also, $\Gamma_{SW} = \frac{1}{3}\Gamma_{GT}$, according to (7) and (12). In the SW theory, however, Γ_{SW} is a measure of the volume dependence of the Néel-temperature function $T_N(\omega)$, according to (3). When the SW theory is used to analyse the magnetoelastic behaviour of Cr alloys (Alberts 1989a), Γ_{SW} is compared with Γ_N, which is determined directly from the volume dependences of the Néel temperature, $\Gamma_N = -\mathrm{d}(\ln T_N)/\mathrm{d}\omega$. In some cases there is rough correspondence between Γ_{SW} ($= \frac{1}{3}\Gamma_{GT}$) and Γ_N, e.g., in Cr (Fawcett 1989a) and in Cr–Mo and Cr–Al alloys (see figures 2 and 4). In other cases, Γ_{NT} is closer to Γ_N than is Γ_{SW}, e.g., in Cr–Ge and Cr-Ga alloys (Fawcett and Alberts 1991).

This rough correspondence between the zero-temperature magnetic Grüneisen parameter (either Γ_{SW} or Γ_{GT}) and Γ_N seems to validate the connection made in the SW theory between the prefactor φ in the magnetic free energy and the Néel-temperature function $T_N(\omega)$, though not perhaps in the explicit form of (1). This feature of the SW theory should be incorporated in the GT theory. This will not however resolve the puzzling fact that in the Cr–Al system, as seen in figure 4, the concentration dependence of Γ_{NT} is completely different from that of Γ_N. One might have expected these two magnetic Grüneisen parameters to be roughly equal, or at least to vary with composition in a similar way.

Another general result, with only one exception, is that the value of the magnetic Grüneisen parametric Γ_{SF} in the paramagnetic phase drops rapidly when the solute is first introduced into Cr. This was first remarked in the Cr–V system (Fawcett 1989d), where about 0.6 at.% V reduces Γ_{SF} by a factor three, from its large value, $\Gamma_{SF} = -150$, in pure Cr. The initial decrease of Γ_{SF} with solute concentration is slow with Mo (figure 2) but very rapid in the case of Ge and Ga (Fawcett and Alberts 1990). The apparent exception to the rule is Al (figure 4), but the gigantic peak seen in the Cr–Al system near the triple point may mask the effect, if the approach to the peak starts when Al is first introduced into Cr.

The gigantic value of the Grüneisen parameter Γ_{SF} at the peak of the singular region in figure 4, at the composition of about Cr + 2.2 at.% Al, is an extreme case of the general rule that Γ_{SF} is usually somewhat larger that Γ_{NT} in pure Cr and in Cr alloys. Thus for Cr, $\Gamma_{SF} \simeq 3\Gamma_{NT}$ (Muir *et al* 1987a, Fawcett 1989a), while figure 2 shows that, for Cr–Mo alloys, $\Gamma_{SF} \simeq 4\Gamma_{NT}$.

Finally, we draw attention to the general result that the various magnetic Grüneisen parameters in the Cr alloy systems considered here are all negative. A more directly physical way of stating this result is that all SDW alloys of Cr, like Cr itself, exhibit a depression of the bulk modulus relative to its value in the non-magnetic alloys, and a monotonically increasing magnetovolume with decreasing temperature.

In this more general form, the result that the volume dependence of the various magnetic characteristic energies is positive, even in cases where it is not possible to define a magnetic Grüneisen parameter, seems to be true for all Cr alloy systems whose magnetoelastic properties have been measured (Alberts 1989a).

In pure Cr, all the magnetic Grüneisen parameters are also negative (Fawcett 1989a), for reasons that are not at all well understood. A plausible explanation, which however remains unproven, is that the exchange interaction parameter I decreases with increasing volume (Kaiser and Haines 1985), with a logarithmic derivative of order unity, i.e., $\mathrm{d}(\ln I)/\mathrm{d}\omega \simeq -1$. Similar behaviour is apparently seen in Pd–Rh alloys, Ni and Ni_3Al (Fawcett *et al* 1986a).

We now consider the behaviour of the specific Cr alloy systems. Ström-Olsen and Wilford (1980) showed, by studying the temperature dependence of the electrical resistivity, that the ordering in Cr–Mo alloys, for compositions up to about 10 at.% Mo, obeys the same law of corresponding states as that in pure Cr. Beyond 10 at.% Mo the ordered state is significantly different from that of Cr, and shows evidence for there being no energy gap. Accordingly, it is not surprising to find in figure 2 a monotonic decrease with increasing Mo concentration for two of the magnetic Grüneisen parameters, Γ_{NT} and Γ_{SF}.

The amazing behaviour of the Cr–Al system, illustrated in figure 4, is not at all understood. The most remarkable features of the magnetoelastic properties are the close correspondence of Γ_{GT} and Γ_{SF}, as functions of Al concentration, throughout the singular region centred on Cr + 2.2 at.% Al, and the absence of any such peak in Γ_{NT}. This is quite unexpected. Why should the zero-temperature magnetic Grüneisen parameter Γ_{GT} be related to the spin-fluctuation parameter Γ_{SF}, rather than to the ordered state parameter Γ_{NT}?

The explanation may be related to the apparent dependence on tetragonal strain of the magnetic properties of Cr–Al alloys having a composition near the triple point. Thus Alberts (1989b) finds that a single crystal, Cr + 2.6 at.% Al, shows a cusp anomaly in the shear constant, $\frac{1}{2}(c_{11} - c_{12})$, with a drop of about 3% (which is to be compared with the drop of about 30% in c_{11} and therefore in B) as temperature decreases through T_N. A similar effect is however seen in pure Cr in the poly-$\boldsymbol{Q}$ state (Van Rijn and Alberts 1983), but not in the single-$\boldsymbol{S}$, single-$\boldsymbol{Q}$ state (Muir *et al* 1987a,b). It would clearly be desirable to measure the elastic constant tensor and the uniaxial thermal expansivities of this sample in the single-$\boldsymbol{Q}$ state. It is not known, however, whether field cooling is effective at a Néel transition to the CSDW state.

While Cr–Al alloys show no anomaly in the polycrystalline shear modulus G at the Néel transition, this is not the case in other systems. Thus the Néel transition to the CSDW state in polycrystalline alloys of Cr–Si (Alberts and Lourens 1988) and Cr–Fe (Hausch and Török 1977) is quite different from the transition to the ISDW state. In both systems the paramagnetic–commensurate (PC) transition is strongly first order, while the paramagnetic–incommensurate (PI) transition is apparently continuous (or perhaps weakly first order as in pure Cr). At the PI transition, the polycrystalline shear modulus G is continuous, as in pure Cr and in most dilute alloys of Cr, while at the strongly first order PC transition G shows a discontinuity. It would clearly be of interest to determine the concentration dependence of the magnetic Grüneisen parameters through the triple-point region in single-Q samples of these alloys, to see whether the dependence of magnetic properties on shear strain has a significant effect.

5. Conclusion

The GT method of analysing magnetoelastic data for Cr alloy SDW systems seems to be most successful in parametrising their behaviour. The results in some cases are very surprising. In particular, the correlation in the Cr–Al system between the magnetic Grüneisen parameters, Γ_{GT} at zero temperature, and Γ_{SF} in the paramagnetic phase, and the lack of correlation of either with Γ_{NT} in the ordered state, are difficult to understand.

Other unsolved problems include the fact that the volume dependence of the magnetic properties in the paramagnetic phase is usually somewhat larger than in the ordered state, i.e., $\Gamma_{SF} > \Gamma_{NT}$. A related effect is the decrease of Γ_{SF} from its high value in pure Cr, when the solute is first introduced.

We should not, however, expect a phenomenological theory to provide microscopic explanations of physical phenomena. We find that the considerable body of experimental knowledge about the magnetoelastic properties of Cr and its dilute antiferromagnetic alloys can largely be expressed in terms of various magnetic Grüneisen parameters. The task of the theorist is now to provide a microscopic theory of these parameters.

Acknowledgments

This work was performed during a visit by one of the authors (EF) to the Rand Afrikaans University. The visit was funded by the Foundation for Research and Development at the Council for Scientific and Industrial Research (Republic of South Africa).

Endorsement

One of the authors (EF) wishes to make explicit his intention that no agency should derive military benefit from the publication of this paper. Authors who cite this work in support of their own are requested to qualify similarly to the availability of their results.

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