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Magnetic Grüneisen parameters in chromium

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Abstract. Grüneisen parameters are defined and determined for Cr in the paramagnetic phase, at and below the Néel temperature, at low temperatures and at zero temperature, by comparing the temperature dependence of the thermophysical properties, as well as from direct pressure measurements (the latter also for dilute antiferromagnetic alloys of Cr with V or Mo). The values are all large and negative, and in particular in the paramagnetic phase the logarithmic volume dependence of the characteristic spin fluctuation temperature is 155.

1. Introduction

The Grüneisen parameters of a magnetic system may be defined as the negative of the logarithmic derivatives with respect to strain of the characteristic energies of the system. For example, for an antiferromagnet, the Grüneisen parameters may be defined for the Néel temperature T_N, and for the square of the sublattice magnetisation M_0 at zero temperature (or equivalently $\frac{1}{2}M_0^2$, where M_0 is the amplitude of a spin-density wave).

Other Grüneisen parameters may be defined in different temperature regions by comparing the magnetic contributions to various thermophysical properties, namely the specific heat, the thermal expansivity and the elastic moduli. For example, for an antiferromagnet, the Grüneisen parameters may be defined below T_N, where the magnetic contributions are associated with the growth of the order parameter with decreasing temperature, and above T_N where the magnetic contributions due to spin fluctuations in the paramagnetic state normally decrease with increasing temperature.

These latter Grüneisen parameters may also be expressed in terms of the temperature dependence of a characteristic energy, if they are analysed in terms of an appropriate model Thus the temperature may be referred to a strain-dependent parameter T_N, or the field energy may be referred to a strain-dependent parameter M_0^2. The analysis normally assumes linearity in the strain dependence. If the system exhibits little anisotropy, it is sufficient to define the Grüneisen parameters in terms of volume strain, with considerable simplification of the formalism.

For the following reasons, Cr and its dilute antiferromagnetic alloys constitute an ideal system to illustrate how in practice these various Grüneisen parameters may be determined.

(i) The Grüneisen parameters are large—the magnetic properties of Cr are very strain dependent.

(ii) The strain dependence is largely a volume dependence—the magnetoelastic tensor of Cr is almost isotropic and the off-diagonal shear components are small.

(iii) A dilute alloy $Cr_{95}V_5$ is available, which does not order magnetically, but which otherwise might be expected to be close to Cr—thus, $Cr_{95}V_5$ may be regarded as 'paramagnetic Cr', to which antiferromagnetic Cr may be referred in order to obtain by subtraction the magnetic contributions to the thermophysical properties.

2. Theory

We shall consider three temperature regions. The first, $T/T_N \lesssim 1$, was analysed by Muir *et al* (1987a)† for the general case, in which the Néel temperature $T_N(\varepsilon_i)$ is linearly dependent on the strain tensor ε_i. Their measurements (Muir *et al* 1987b) of the temperature dependence of the elastic constants of single-*S* single-*Q* Cr show that the magnetic contribution corresponds, to a good approximation, to a dependence on volume strain ω. In this approximation, the magnetic free energy in the ordered state close to the Néel temperature may be written

$$\Delta F(t) = f[t(\omega)] \qquad t(\omega) = T/T_N(\omega) \lesssim 1. \tag{1}$$

This gives for the ratios of the magnetic contributions to the specific heat C, the thermal expansivity β and the bulk modulus B, the expressions

$$\frac{\Delta\beta(t)}{\Delta C(t)} = -\frac{1}{B(t)}\frac{\mathrm{d}\ln[T_N(\omega)]}{\mathrm{d}\omega}\frac{[f'(t)+tf''(t)]}{tf''(t)} \tag{2}$$

$$\frac{\Delta B(t)}{\Delta\beta(t)} = T_N B(t)\frac{\mathrm{d}\ln[T_N(\omega)]}{\mathrm{d}\omega}t\frac{[2f'(t)+tf''(t)]}{[f'(t)+tf''(t)]}. \tag{3}$$

The function $f(t)$ might be expected to resemble the order parameter, which is a rapid function of t close to T_N (see figure 4(*a*) in the paper by Fawcett (1988)), so that $f'(t)$ may be neglected relative to $f''(t)$. In this approximation, we obtain the Grüneisen parameters

$$\Gamma^{I}_{-} = B_N \lim_{t\to 1}[\Delta\beta(t)/\Delta C(t)] \tag{4}$$

$$\Gamma^{II}_{-} = -(1/T_N B_N)\lim_{t\to 1}[\Delta B(t)/\Delta\beta(t)] \tag{5}$$

where B_N is the bulk modulus at T_N. For this model, the two Grüneisen parameters have the same value

$$\Gamma^{I}_{-} = \Gamma^{II}_{-} = -\mathrm{d}\{\ln[T_N(\omega)]\}/\mathrm{d}\omega. \tag{6}$$

We consider next the temperature region close to, but above, the Néel temperature: $t = T/T_N \gtrsim 1$. Here spin fluctuations are assumed to make a contribution to the magnetic free energy similar in form to equation (1):

$$\Delta F(t) = g[t(\omega)] \qquad t(\omega) = T/T_{SF}(\omega) \gtrsim 1. \tag{7}$$

The temperature here is referred to a spin-fluctuation temperature $T_{SF}(\omega)$, whose strain dependence may be quite different from that of $T_N(\omega)$. The function $g(t)$ might be

† Note that in the present paper a different notation is used for the Grüneisen parameters, since in Fawcett *et al* (1986a) and in this reference the distinction between the first and second kind, Γ^{I} and Γ^{II}, respectively, is obscure; thus $\gamma_{TN-} \equiv \Gamma^{I}_{-}$, $\gamma^{-}_{TN} \equiv \Gamma^{II}_{-}$, $\gamma_{TN+} \equiv \Gamma^{I}_{+}$, $\gamma^{+}_{TN} \equiv \Gamma^{II}_{+}$ and $\gamma_{TN} \equiv \Gamma_N$.

expected to resemble the temperature dependence of the mean square magnetic moment of the spin fluctuations, varying rapidly close to T_N, so that $g'(t)$ may be neglected relative to $g''(t)$, like the approximation for $f(t)$ when $t \leqslant 1$. Thus the resultant expressions, analogous to equations (2) and (3), yield Grüneisen parameters Γ_+^{I} and Γ_+^{II} defined by equations such as (4) and (5), but with t approaching the limit 1 from above, i.e. $t \geqslant 1$. For this model, one obtains

$$\Gamma_+^{\mathrm{I}} = \Gamma_+^{\mathrm{II}} = -\mathrm{d}\{\ln[T_{\mathrm{SF}}(\omega)]\}/\mathrm{d}\omega. \tag{8}$$

We consider finally the low-temperature region, where two strain-dependent parameters are needed to describe the magnetic free energy. We shall see in § 3 that three parameters can be determined from the available experimental data for Cr. Γ_0^{I} and Γ_0^{II} are defined by equations like the Grüneisen parameters defined close to T_N by equations (4) and (5), which are the temperature-dependent contributions to the thermo-physical properties in the limit as temperature tends to zero. Γ_0^{III} is defined, on the other hand, at zero temperature, by the ratio of the fractional change in the bulk modulus to the magnetovolume:

$$\Gamma_0^{\mathrm{III}} = (1/B_0)(\Delta B_0/\Delta\omega_0). \tag{9}$$

The magnetic contributions to the bulk modulus and the magnetovolume at zero temperature may be included in the formalism by introducing a volume-dependent pre-factor $\varphi(\omega)$ into the magnetic contribution to the free energy. The temperature dependence at low temperatures is described by defining the reduced temperature in terms of a volume-dependent temperature parameter $T_0(\omega)$ characteristic of the low-temperature region. Thus, we write

$$\Delta F(T, \omega) = \varphi(\omega) f[t(\omega)] \qquad t(\omega) = T/T_0(\omega) \geqslant 0 \tag{10}$$

and obtain the following expressions for the thermophysical properties:

$$\Delta C = -T[\partial^2(\Delta F)/\partial T^2] = -\varphi t f''/T_0 \tag{11}$$

$$\Delta\omega = -(1/B)[\partial(\Delta F)/\partial\omega] \simeq (1/B_0)\{\varphi[\mathrm{d}(\ln T_0)/\mathrm{d}\omega]tf' - \varphi' f\} \tag{12}$$

$$\Delta\beta = \partial(\Delta\omega)/\partial T \simeq (1/B_0 T_0)\{\varphi[\mathrm{d}(\ln T_0)/\mathrm{d}\omega](f' + tf'') - \varphi' f'\} \tag{13}$$

$$\begin{aligned}\Delta B = \partial^2(\Delta F)/\partial\omega^2 = {} & \varphi'' f \\ & - 2\varphi'[\mathrm{d}(\ln T_0)/\mathrm{d}\omega]tf' + \varphi[\mathrm{d}(\ln T_0)/\mathrm{d}\omega]^2(2tf' + t^2 f'').\end{aligned} \tag{14}$$

In equations (12) and (13), we take B to be constant and equal to the zero-temperature value B_0, since the temperature dependence of the bulk modulus can be shown to make a negligible contribution to $\Delta\beta$ in Cr, because of the small value of the zero-temperature magnetovolume $\Delta\omega_0$. In equation (14), we have assumed $T_0(\omega)$ to be a linear function of ω, so that its second derivative is negligible, in contrast with $\varphi(\omega)$, whose second derivative is entirely responsible for the magnetic contribution to the zero-temperature bulk modulus.

The analysis is able to proceed only by use of a reasonable, but rather crude, approximation for the function $f(t)$ in the low-temperature limit, namely

$$f(t) \simeq 1 \qquad tf''(t) = f'(t) \simeq t. \tag{15}$$

These approximations are true in the low-temperature limit of, for example, the function $f(t) = (1 - t^2)^2$ used by Testardi (1975) to illustrate his thermodynamic analysis for a general ordering transition, and by Steinemann (1978) for the free energy of a weak itinerant antiferromagnet.

We then obtain, writing

$$x = -\mathrm{d}(\ln T_0)/\mathrm{d}\omega \qquad y = -\mathrm{d}(\ln \varphi)/\mathrm{d}\omega \tag{16}$$

expressions for the three low-temperature parameters:

$$\Gamma_0^{\mathrm{I}} = B_0 \lim_{t\to 0}[\Delta\beta(t)/\Delta C(t)] = 2x - y \tag{17}$$

$$\Gamma_0^{\mathrm{II}} = -(1/B_0 T_0) \lim_{t\to 0}[\Delta B(t)/t\Delta\beta(t)] = (3x^2 - 2y)/(2x - y) \tag{18}$$

$$\Gamma_0^{\mathrm{III}} = (1/B_0)(\Delta B_0/\Delta\omega_0) = -\mathrm{d}(\ln \varphi')/\mathrm{d}\omega = -\varphi''/\varphi'. \tag{19}$$

Only Γ_0^{III} is a Grüneisen parameter in the sense that we are using the term, namely the negative of the logarithmic derivative with respect to volume strain of a characteristic energy of the system (or more precisely, in this case, the volume strain derivative of such an energy). x and y, as defined in equation (16), are also low-temperature Grüneisen parameters, which are obtained by solving equations (17) and (18) with the measured values of the pseudo-Grüneisen parameters Γ_0^{I} and Γ_0^{II}.

3. Experiment

The volume thermal expansivity β and the bulk modulus B of Cr, when compared with those of $Cr_{95}V_5$, as illustrated in figures 1 and 2, respectively, show strong magnetic contributions. In each case, the magnetic contribution in the paramagnetic phase above the Néel temperature T_N is comparable in magnitude with that seen below T_N and persists up to about 600 K for β and up to somewhat higher temperatures for B.

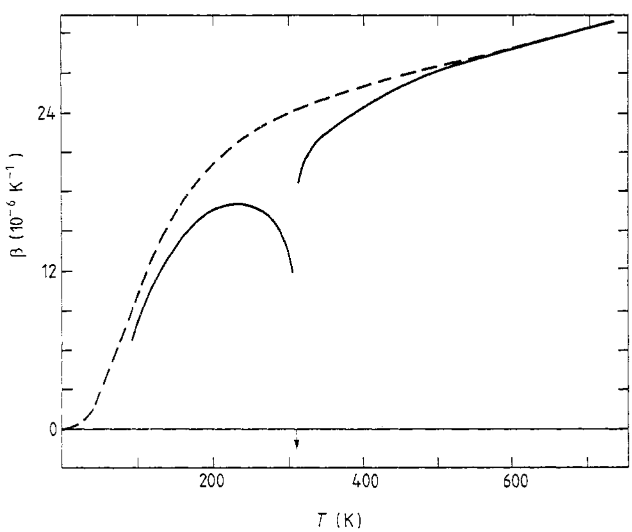

Figure 1. Temperature dependence of the volume thermal expansivity of Cr (——) and $Cr_{95}V_5$ (---). The negative thermal expansivity due to the first-order Néel transition in Cr is shown by an arrow at the Néel temperature $T_N \simeq 311$ K (after Roberts *et al* (1983) and White *et al* (1986)).

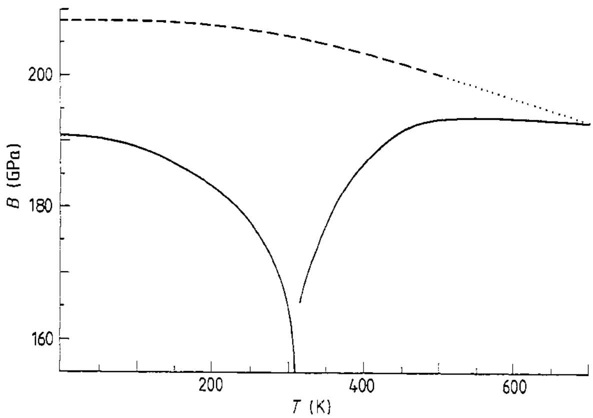

Figure 2. Temperature dependence of the bulk modulus of Cr (——) and $Cr_{95}V_5$ (– – –) in the temperature range $T = 0$–700 K. The curve for Cr below the Néel temperature $T_N \simeq 311$ K is obtained from the data of Muir *et al* (1987b) and above T_N from Lähteenkorva and Lenkkeri (1981). The curve for $Cr_{95}V_5$ is obtained from the data of Alberts and Lourens (1985) and Alberts (1987) and is adjusted by shifting in the direction of the ordinate axis so as to intersect the curve for Cr at the temperature $T = 700$ K, the highest measured.

When we plot the magnetic contribution to the bulk modulus

$$\Delta B = B(\mathrm{Cr}) - B(\mathrm{Cr}_{95}\mathrm{V}_5) \tag{20}$$

against the magnetic contribution to the thermal expansivity

$$\Delta\beta = \beta(\mathrm{Cr}) - \beta(\mathrm{Cr}_{95}\mathrm{V}_5) \tag{21}$$

we expect from equation (3) to find that, as the temperature approaches the Néel transition from below, making $f'(t) \ll f''(t)$, linearity between $\Delta\beta$ and ΔB will be observed. In fact, the linearity is found to extend over a very wide temperature range, from a temperature T a little below $T_N \simeq 311$ K, at least down to $T = 130$ K (see figure 2 in Muir *et al* (1987a)). Over this range, the bulk modulus of $Cr_{95}V_5$ varies by less than 1% (Alberts and Lourens 1985, Alberts 1987) and, using its value at the Néel temperature, $B_N = 207$ GPa, in equation (5), we obtain from the proportionality factor between ΔB and $\Delta\beta$ a Γ^{II}_{-} value of -37 for the Grüneisen parameter. A better Γ^{II}_{-} value of -40 is obtained by using $B_N = 190$ GPa, the rough average of B_N for $Cr_{95}V_5$ and Cr near $T_N = 311$ K (see figure 2).

Note that ΔB and $\Delta\beta$, as defined in equations (20) and (21), are both negative and opposite in sign to the corresponding quantities obtained by Muir *et al* (1987a). It was convenient in this earlier paper to follow Testardi (1975) and to define $-\Delta F(t)$ as the magnetic contribution to the free energy. This makes no difference to the signs of the Grüneisen parameters, since each is defined in equations (4), (5) and (9) as the *ratio* of the magnetic contributions to two thermophysical properties.

We find furthermore that ΔB and $\Delta\beta$ are linearly related above the Néel transition, from a temperature a little above T_N, up to at least $T = 500$ K (see figure 2 in Muir *et al* (1987a)). The rate of change in ΔB with temperature relative to that of $\Delta\beta$ in the paramagnetic phase is considerably greater, however, than in the ordered phase, and the analogue of equation (5) for $t > 1$ gives a Γ^{II}_{+} value of -155 for the Grüneisen parameter, with $B_N = 190$ GPa.

Because of these large values of the Grüneisen parameters, it is difficult to obtain meaningful values for Γ^{I}_{-} and Γ^{I}_{+} by the use of equation (4) and its analogue for $t \geqslant 1$. Thus, even with very careful absolute calorimetry, the magnetic contribution ΔC to the specific heat can be determined with only poor accuracy. Below the Néel transition, in the data of Williams *et al* (1979) for Cr and for $Cr_{99.5}V_{0.5}$ (whose Néel temperature is about 50 K below that of Cr, so that it constitutes a satisfactory reference material), we obtain, at $T = 300$ K, a magnetic contribution to the specific heat ΔC of about 23 kJ m^{-3} (see figure 2 of Fawcett *et al* (1986a)). The corresponding magnetic contribution $\Delta\beta$ to the thermal expansivity of about 10×10^{-6} K^{-1} gives, with $B_N = 190$ GPa in equation (4), a Γ^{I}_{-} value of -65 for the Grüneisen parameter.

In the paramagnetic phase, the magnetic contribution to the thermal expansivity, as seen in figure 1, is somewhat smaller than in the ordered phase, and the Grüneisen parameter is so large that the specific heat of Cr coincides, within the experimental accuracy of 0.2%, with that of $Cr_{99.5}V_{0.5}$ (see figure 2 of Fawcett *et al* (1986a)). Thus only a lower limit is available for its magnitude: $|\Gamma^{\mathrm{I}}_{+}| \geqslant 100$.

In the low-temperature region, we shall consider the behaviour of $Cr_{100-x}V_x$ alloys, as well as that of Cr. The coefficient of the linear term in the temperature dependence of the thermal expansivity and the specific heat of Cr, given in table 1, were used by Kaiser *et al* (1985) to determine an 'electronic' Grüneisen parameter defined by analogy with equation (2):

$$\Gamma_e = B_0(\beta(t)/C(t) \tag{22}$$

which has essentially the same value, $\Gamma_e \simeq -12 \pm 1$, for the antiferromagnetic alloys as for Cr. If, however, in the spirit of equation (1), we define magnetic contributions to β and C by writing

$$\Delta\beta = \beta(\mathrm{A}) - \beta(\mathrm{Cr_{95}V_5}) \tag{23}$$

$$\Delta C = C(\mathrm{A}) - C(\mathrm{Cr_{95}V_5}) \tag{24}$$

where $\beta(\mathrm{A})$ and $C(\mathrm{A})$ correspond to the antiferromagnetic alloy A, containing $x < 5$ at.% V ($x = 0$ for Cr), we obtain the low-temperature Grüneisen parameter Γ^{I}_0 defined in equation (17). The values of Γ^{I}_0 in table 1 are all *positive* and range from 23 for Cr to 142 for Cr–3.4 at.% V.

We now consider Γ^{II}_0 for Cr, as defined in equation (18). This can be obtained from the temperature dependence of the magnetic contributions to the thermal expansivity,

Table 1. Low-temperature Grüneisen parameters Γ_e ('electronic' defined in equation (22)), and Γ^{I}_0 (defined in equation (17)) of Cr and dilute $Cr_{100-x}V_x$ alloys. Data are taken from table 1 of Kaiser *et al* (1985), and the Grüneisen parameters were calculated by use of the average value $B_0 = 200$ GPa for the bulk modulus (see figure 2).

x (at.% V)	T_N (K)	β/T (10^{-9} K^{-2})	$\Delta\beta/T$ (10^{-9} K^{-2})	C/T (J m^{-3} K^{-2})	$\Delta C/T$ (J m^{-3} K^{-2})	Γ_e	Γ^{I}_0
0	311	−10.8	−14.1	200	−120	−11	23
0.5	263	−11.4	−14.7	210	−110	−11	27
1.5	150	−15.0	−18.3	220	−100	−13	37
2.5	105	−15.6	−18.9	250	−70	−12	54
3.4	28	−18.0	−21.3	290	−30	−12	142
5	0	3.3		320		2.0	

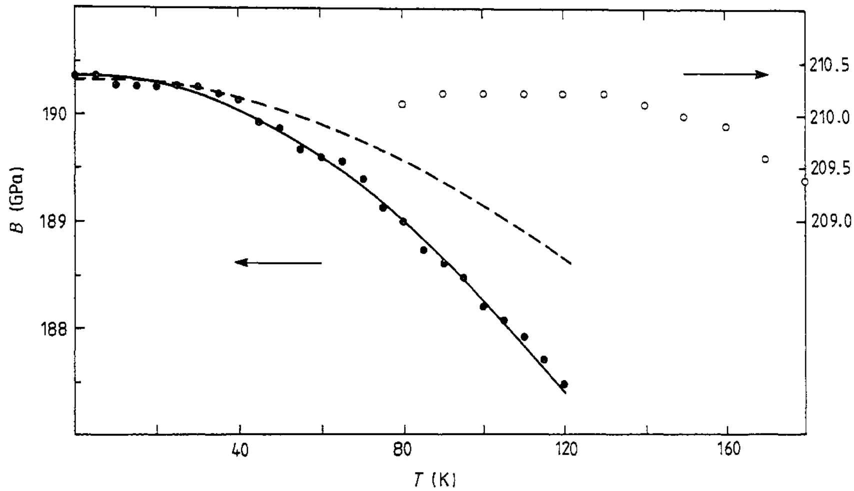

Figure 3. Temperature dependence of the bulk modulus of Cr (●) and $Cr_{95}V_5$ (○) in the temperature range $T = 0$–180 K in which the Cr values are calculated from the data of Palmer and Lee (1971) for a Cr single crystal, and the $Cr_{95}V_5$ values were measured on a polycrystalline sample by Alberts (1987): ——, quadratic least-squares fit over the temperature range $T = 5$–120 K; ---, fit over the range $T = 5$–40 K.

$\Delta\beta(T)/T$, given in the first column of table 1, and to the bulk modulus $\Delta B(T)$. Evaluation of $\Delta B(T)$ from the available low-temperature data, shown in figure 3, is difficult. The bulk modulus of $Cr_{95}V_5$ appears to be constant below about 130 K. Although the measurements terminate at 80 K, it seems unlikely that there will be any further variation at lower temperatures. For Cr, however, while the quadratic fit

$$B(T) = B_0 + B_2T^2 \qquad B_0 = 190.4\ \text{GPa} \qquad B_2 = -207\ \text{kPa K}^{-2} \tag{25}$$

to the temperature dependence of $B(T)$ is quite good over the whole temperature range below the spin-flip temperature $T_{SF} \simeq 123$ K, the coefficient $B_2 = -116$ kPa K^{-2} is significantly smaller for a fit over the temperature range $T = 5$–40 K. One cannot rule out indeed the possibility that, below $T = 20$ K, B_2 is zero within the experimental accuracy. Thus, we obtain two values: $\Gamma_0^{II} = -73 (T \leqslant 120\ \text{K})$ or $\Gamma_0^{II} = -41\ (T \leqslant 40\ \text{K})$.

Equations (17) and (18) yield a quadratic equation for x (or y), as defined in equation (16), which has two solutions for each value of B_2 and Γ_0^{II}, as given in table 2. Since the volume derivatives of $T_{SF}(\omega)$ and $T_N(\omega)$ in table 4 (see later) are both positive, it seems unlikely that the solution of the quadratic equation corresponding to the negative values for $\mathrm{d}(\ln T_0)/\mathrm{d}\omega$ and $\mathrm{d}(\ln \varphi)/\mathrm{d}\omega$ in table 2, labelled (*a*) and (*c*), are relevant to Cr. We adopt the values labelled (*b*), but we must keep in mind the possibility that a fit to $B(T)$

Table 2. Low-temperature Grüneisen parameters in Cr, rounded off to the nearest multiple of 5.

B_2 (kPa K^{-2})	$x = -\mathrm{d}(\ln T_0)/\mathrm{d}\omega$	$y = -\mathrm{d}(\ln \varphi)/\mathrm{d}\omega$	Γ_0^{III}
-207 ($T \leqslant 120$ K)	(*a*) 70	120	-70
	(*b*) -25	-70	
-116 ($T \leqslant 40$ K)	(*c*) 60	100	
	(*d*) -15	-55	

at lower temperatures might give the solutions labelled (*d*) in table 2, or even smaller values $d(\ln T_0)/d\omega \leqslant 15$ and $d(\ln \varphi)/d\omega \leqslant 55$.

The Γ_0^{III} value of -70, is obtained from the values $\Delta B_0 = -20$ GPa and $B_0 = 200$ GPa, the latter being the average value for the bulk modulus at zero temperatures for Cr and $Cr_{95}V_5$, as seen in figure 3, with the magnetovolume $\Delta\omega_0 = 1.43 \times 10^{-3}$ (Kaiser *et al* 1985) substituted in equation (9).

The commonest Grüneisen parameter in a magnetic system is derived from direct measurement of the pressure dependence of the ordering temperature T_N, with

$$\Gamma_N = -d(\ln T_N)/d\omega = B_N[d(\ln T_N)/dp]. \tag{26}$$

The negative sign in equation (26) ensures consistency, according to equation (6), with the Grüneisen parameters Γ_-^I and Γ_-^{II} defined in equations (4) and (5). In table 3, the magnitude of Γ_N for dilute alloys of Cr having $T_N \geqslant 200$ K is roughly constant. It increases rapidly, however, for lower values of T_N, e.g. Γ_0^I in table 1. Γ_0^I is positive however, and it would be necessary for each alloy to combine the value of Γ_0^I with the corresponding value of Γ_0^{II} to obtain $d(\ln T_0)/d\omega$, as shown for Cr in table 2, before a comparison could be made with $d(\ln T_N)/d\omega$.

Finally, we can define another Grüneisen parameter based on direct pressure measurements on Cr. The magnitude of the wave-vector Q of the spin-density wave decreases under pressure. The pressure dependence can be measured accurately by a de Haas–van Alphen technique (Venema *et al* 1980), and Ruesink and Templeton (1984) have studied the remarkable hysteretic effects which are thought to be due to pinning of the spin-density wave by impurities (Fawcett 1988). The 'soft mode', which is observed when pressure is applied after first cooling, is believed to be the intrinsic behaviour and Ruesink and Templeton (1984) determined a value for the pressure dependence under these conditions: $d(\ln Q')/dp = -5.5 \pm 0.3\ \mathrm{TPa}^{-1}$, where $Q' = Qa/2\pi$ is the magnitude of Q measured in units of the reciprocal lattice vector.

The appropriate quantity for determining the Grüneisen parameter Γ_Q, however, is $\delta' = 1 - Q'$, the incommensurability parameter. The relation (Venema *et al* 1980)

$$d(\ln \delta')/d\omega = B_0[d(\ln Q')/dp][(1-\delta)/\delta] - \tfrac{1}{3} \tag{27}$$

gives the value

$$\Gamma_Q = d\{\ln[(\delta')^2]\}/d\omega = -42 \pm 2 \tag{28}$$

Table 3. Grüneisen parameters Γ_N for Cr and its dilute antiferromagnetic alloys, obtained from the pressure dependence of the Néel temperature T_N. An average value for the bulk modulus $B_N = 180$ GPa is assumed for use in equation (26). Note that the sign of $d(\ln T_N)/dp$ was wrong throughout in the original version of this table (Fawcett *et al* 1986b).

Reference	x (at.%)	T_N (K)	$d(\ln T_N)/dp$ (TPa^{-1})	$\Gamma_N = -d(\ln T_N)/d\omega$
McWhan and Rice (1967)	0	311	−1.65	−29
Furuya *et al* (1970)	1.18Mn + 0.59V	433	−1.5	−26
Furuya *et al* (1970)	0.45V		−1.6	−28
Rice *et al* (1969)	8.6Mo	208	−1.45	−26
Rice *et al* (1969)	1.2V	200	−1.25	−23
Rice *et al* (1969)	12Mo	144	−2.2	−40
Rice *et al* (1969)	2.8V	92	−3.15	−57

when we substitute the low-temperature values $\delta = 0.0486$ and $B_0 = 190$ GPa. Equation (28) follows from Walker's (1980) phenomenological Landau-type theory of the spin-density wave state of Cr. He shows that the Gibbs free energy is quadratic in δ', with a negative sign corresponding to the requirement that the minimisation of this term with respect to δ' should give a non-zero value of δ', i.e. an incommensurate spin-density wave.

4. Discussion

We assemble in table 4 the values of the Grüneisen parameters for Cr for the different temperature regions, obtained by the various experimental procedures. All the values of the corresponding logarithmic derivatives of the characteristic energies are positive, except $\mathrm{d}\{\ln[(\delta')^2]\}/\mathrm{d}\omega$. We have bracketed the values of Γ_0^{II} and Γ_0^{I}, since they are pseudo-Grüneisen parameters, and algebraic analysis is required to obtain from them the Grüneisen parameters $-\mathrm{d}(\ln T_0)/\mathrm{d}\omega$ and $-\mathrm{d}(\ln \varphi)/\mathrm{d}\omega$ given in the last column of table 4. The alternative choice of the root of the quadratic equation, however, would yield positive values for these Grüneisen parameters, as seen from line (*a*) of table 2. Also a fit to the low-temperature data ($T \leqslant 40$ K) in figure 3 yields values of these Grüneisen parameters somewhat smaller in magnitude, as in line (*d*) of table 2.

The magnitude of the Grüneisen parameter $\Gamma_+^{\mathrm{II}} = -155$ in the paramagnetic phase is at least a factor of 2 greater than that of any other Grüneisen parameter in the ordered phase. The significance of this giant Grüneisen parameter in paramagnetic Cr is discussed elsewhere (Fawcett 1988b). It may be characteristic of the spin fluctuations responsible for the commensurate diffuse (CD) inelastic neutron scattering seen by Grier *et al* (1985) in Cr. The Γ_+^{II} value of -55 in the dilute alloy Cr–(0.5–0.67) at.% V is considerably smaller (Fawcett 1989), and the CD scattering is suppressed in these $Cr_{100-x}V_x$ alloys (Fawcett *et al* 1988, 1989).

There have been several calculations of the magneto-elastic coupling constant C in Cr, which relates the magnetovolume strain ω to the mean square moment $\langle M^2(T)\rangle$ through the equation

$$\omega = (C/B)\langle M^2\rangle. \tag{29}$$

At zero temperature, the ground-state magnetovolume strain ω_0 for a spin-density wave of amplitude M_0 is

$$\omega_0 = \tfrac{1}{2}(C/B_0)M_0^2. \tag{30}$$

Kaiser and Haynes (1985) quote several theoretical estimates which use either calculated or experimental values of M_0 to yield values over the wide range $C/B_0 = 0.8$ to

Table 4. Values of the Grüneisen parameters, and best values for the logarithmic derivatives of the characteristic energies for Cr, rounded off to the nearest multiple of 5.

Paramagnetic phase	$\Gamma_+^{\mathrm{II}} = -155, \Gamma_-^{\mathrm{I}} < -100$	$\mathrm{d}(\ln T_{\mathrm{SF}})/\mathrm{d}\omega = 140$
Néel temperature T_{N}	$\Gamma_{\mathrm{N}} = -30$	$\mathrm{d}(\ln T_{\mathrm{N}})/\mathrm{d}\omega = 30$
Below T_{N}	$\Gamma_-^{\mathrm{II}} = -40, \Gamma_-^{\mathrm{I}} = -65$	$\mathrm{d}\{\ln[T_{\mathrm{N}}(\omega)]\}/\mathrm{d}\omega = 40$
Low temperatures	$(\Gamma_0^{\mathrm{II}} = -73, \Gamma_0^{\mathrm{I}} = 23)$	$\mathrm{d}(\ln T_0)/\mathrm{d}\omega = 25$
		$\mathrm{d}(\ln \varphi)/\mathrm{d}\omega = 70$
	$\Gamma_Q = -40$	$\mathrm{d}\{\ln[(\delta')^2]\}/\mathrm{d}\omega = -40$
Zero temperature	$\Gamma_0^{\mathrm{III}} = -70$	$\mathrm{d}(\ln \varphi')/\mathrm{d}\omega = 70$

$6.6\%\mu_B^{-2}$. Fawcett *et al* (1986a) estimate a C/B_0 value of $0.9\%\mu_B^{-2}$ from their thermal expansion data combined with the measured value of M_0. They suggest that this discrepancy between large theoretical estimates and their relatively low experimental value of C/B_0 are due to the volume dependence of the exchange interaction parameter in Cr.

It is not clear how to relate the theoretical estimates of the magneto-elastic coupling constant to the experimental Grüneisen parameters, however. I recommend to the attention of theorists this problem as well as the problem of explaining, perhaps by use of a phenomenological model, the giant Grüneisen parameter in the paramagnetic phase of Cr.

Endorsement

It is the author's wish that no agency should ever derive military benefit from the publication of this paper. Authors who cite this work in support of their own are requested to qualify similarly the availability of their results.

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