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## REVIEW ARTICLE

# Magnetoelastic anomalies in spin-density-wave Cr alloys

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**Abstract.** Measurements of the thermal expansion and elastic constants of dilute anti-ferromagnetic Cr alloys are reviewed and analysed to obtain the strain dependence of characteristic temperatures (energies) for the Néel transition and the phase transition between the incommensurate (I) and commensurate (C) spin-density-wave (SDW) phases. The results are related where possible to the behaviour of the transition temperatures under pressure, which correspond normally to positive and negative volume dependence, respectively, of the Néel temperature  $T_N$  and the ICSDW phase transition temperature  $T_{IC}$ , as indicated by the minimum at  $T_N$  and maximum at  $T_{IC}$  in the temperature dependence of the thermal expansivity. The unique anomaly in the temperature dependence of the shear strain modulus in CrRu alloys is analysed along the same lines.

## 1. Introduction

The pronounced anomalies in the thermal expansion and elastic constants (in particular, the Young's modulus) of pure Cr that are associated with the magnetic ordering were first observed by Fine *et al* (1951), well before Bacon (1961) discovered the incommensurate spin-density wave (SDW) in this prototypical antiferromagnet. In fact Bridgman (1932), who discovered the phase transition through an anomaly in the temperature dependence of the electrical resistance, also found that the transition temperature  $T_N$  is strongly depressed under pressure. Thus, with the identification of the phase transition with antiferromagnetic ordering by means of neutron diffraction (Shull and Wilkinson 1953), we already knew almost 40 years ago that the magnetoelastic coupling in Cr is strong.

A fundamental microscopic theory for the magnetoelastic properties is still wanting however. The first measurements by Bolef and de Klerk (1963) of the elastic constants of single crystal samples of Cr showed that the magnetoelastic coupling is almost entirely with the volume strain, there being only a negligible contribution from shear strain. The softening of the crystal, shown by a marked decrease in the bulk modulus with magnetic ordering, and the large positive magnetovolume, which was determined by comparison with a paramagnetic alloy of Cr (White *et al* 1986, Fawcett *et al* 1986), are consistent with there being a term in the free energy that is quadratic in the amplitude of the SDW, and that corresponds to a magnetic pressure. Thus the magnetoelastic behaviour of Cr conforms with that predicted by Janak (1977) for all the 3D magnetic metals, within the spin-density-functional approximation (Moruzzi *et al* 1978). Holden *et al* (1984) used this idea to relate the magnetoelastic coupling

in Cr (and Fe and Ni) to the volume dependence of the band structure, on the one hand, and of the exchange interaction parameter, on the other.

A theory for the magnetoelastic coupling is not necessary, however, to validate the use of the anomalies that are often seen in the magnetoelastic properties at the various phase transitions in Cr alloy systems in determining their magnetic phase diagrams. This method has been used, especially by Alberts and coworkers, as referenced in table 1, both to map out the magnetic phase diagram of the Cr alloy system as a function of composition and temperature, and to determine the characteristic features of the magnetoelastic coupling.

The nature of the anomalies in the temperature dependence of the thermal expansivity  $\beta(T)$  and bulk modulus  $B(T)$  is in some cases unique for a range of compositions in a specific Cr alloy system. In most cases, however, both  $\beta(T)$  and  $B(T)$  show a minimum in the neighbourhood of the Néel transition, as shown for example in figure 1, and although, for some alloy compositions, the anomaly is difficult to characterize, it is *never* a maximum.

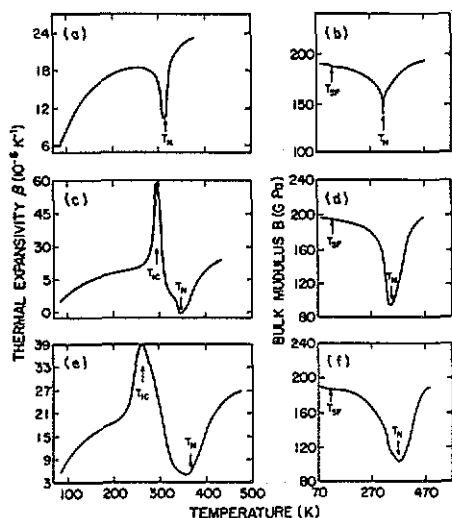


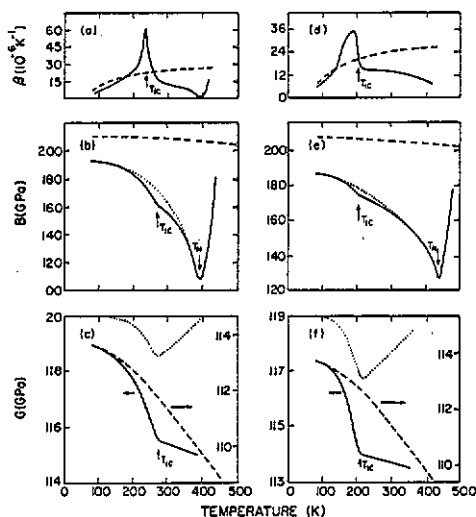
Figure 1. The temperature dependence of the volume thermal expansivity  $\beta$  and bulk modulus  $B$  for three  $\text{Cr}_{1-x}\text{Mn}_x$  alloys containing:  $x = 0.09$  at.% Mn ... (a) and (b);  $x = 0.23$  at.% Mn ... (c) and (d);  $x = 0.33$  at.% Mn ... (e) and (f). The Néel transition temperature  $T_N$  and IC SDW phase transition temperature  $T_{IC}$  are determined from the peaks in  $\beta(T)$ , except for the  $x = 0.09$  at.% Mn sample, which has a sharp minimum in  $B(T)$ . The spin-flip transition between the transverse and longitudinal SDW phases at temperature  $T_{SP}$  is also indicated.

With the exception of CrNi and CrPd, all Cr alloy systems  $\text{Cr}_{1-x}\text{A}_x$  with transition metals A of groups 7 and 8 of the periodic table exhibit a triple point at a concentration  $x_L$  of A, with the Néel transition for  $x > x_L$  being to the commensurate SDW phase. The same is true for alloys with groups 3 and 4 non-transition metals. On further lowering the temperature, in the concentration range,  $x_L < x < x_0$ , there is a transition to the incommensurate SDW phase at temperature  $T_{IC}$ , with  $T_{IC}$  going to zero at  $x = x_0$ . The only exception to this type of behaviour is the CrFe alloy system, for which the commensurate to incommensurate (referred to conventionally as IC) transition occurs with *increasing* temperature, for  $x \lesssim x_L$  (Ishikawa *et al* 1967, Arrott *et al* 1967).

In all systems that have been measured, the thermal expansivity  $\beta(T)$  shows a minimum near the Néel transition from the paramagnetic phase to either the incommensurate or the commensurate SDW phase. The transition at  $T_{IC}$  from the incommensurate to the commensurate SDW phase, on the other hand, either shows a *maximum* in  $\beta(T)$ , as shown for example in figure 1, or in some cases no anomaly

at all is seen at this transition. Again CrFe alloys are exceptional, since they show a strongly first-order hysteretic transition to the commensurate SDW phase from the paramagnetic phase or from the incommensurate SDW phase (Edwards and Fritz 1974, 1975, Fawcett and Vettier 1982)

In most cases, when a maximum in  $\beta(T)$  is seen at  $T_{IC}$ , an anomaly is also seen at this phase transition in the temperature dependence of the bulk modulus  $B(T)$ , which is always a minimum, like that seen at  $T_N$ , though not as pronounced, as shown for example in figure 2. In some cases, when the two phase transition temperatures,  $T_N$  and  $T_{IC}$ , are close, the two minima in  $B(T)$  coalesce to form a single broad minimum, as shown for example in figure 1.



**Figure 2.** The temperature dependence of the thermal expansivity  $\beta$ , the bulk modulus  $B$ , and the shear modulus  $G$  for two  $\text{Cr}_{1-x}\text{Ru}_x$  alloys containing:  $x = 0.3$  at.% Ru ... (a), (b) and (c);  $x = 0.5$  at.% Ru ... (d), (e) and (f). The Néel temperature  $T_N$  and ICSDW phase transition temperature  $T_{IC}$  are determined from the minimum in  $B(T)$  and the maximum in  $\beta(T)$ , respectively. The dash curve shows the temperature dependence of  $\beta$ ,  $B$  and  $G$  for a paramagnetic alloy, Cr + 5 at.% V. In panels (c) and (f), the dash curve is made asymptotic to the continuous curve at low temperature, and the difference at higher temperature, which is shown by the dot curve, is assumed to be the magnetic contribution  $\Delta G(T)$  to the shear modulus. In panels (a) and (d), the magnetic contribution  $\Delta\beta(T)$  to the thermal expansivity is the difference between the dash and continuous curves. In panels (b) and (e), the reference is estimated by the dot curve sketched as shown, and  $\Delta B(T)$  is the difference between this and the continuous curve.

The system CrRu is remarkable in that polycrystalline samples show an anomaly also in the temperature dependence of the shear modulus  $G(T)$  at the IC SDW phase transition, as shown in figure 2. The only other Cr alloy systems that exhibit an anomaly in the shear modulus are CrFe (Hausch and Török 1977) and CrSi (Alberts and Lourens 1988a), where the anomaly is large enough to give a minimum in  $G(T)$ , since it is associated with the strongly first-order transition seen in these systems.

All these experimental observations, which are summarized in table 1, may be understood qualitatively, and in most cases quantitatively, within the framework of the method developed by Fawcett (1989) to describe and analyse the magnetoelastic

properties of pure Cr. This so-called Grüneisen–Testardi (GT) method of analysis was compared with the Stoner–Wohlfarth (sw) method by Fawcett and Alberts (1990), who applied the former to derive magnetic Grüneisen parameters for CrMo and CrAl alloys from the magnetic contributions to their magnetoelastic properties  $\beta(T)$  and  $B(T)$ .

The sw method makes an explicit ansatz for the temperature dependence of the magnetic free energy, but the GT method is quite general and may in principle be applied to the analysis of the IC SDW phase transition, just as well as to the Néel transition, so long as the transition may be assumed to be continuous. Thus the minimum seen in both  $\beta(T)$  and  $B(T)$  around the Néel temperature  $T_N$  follows from the negative sign of the magnetic Grüneisen parameters, including that obtained from the negative pressure-dependence of  $T_N(p)$ , which is seen in all Cr alloy systems that have been measured (as well as in pure Cr), as listed in table 1. In just the same way, the maximum in  $\beta(T)$  and minimum in  $B(T)$  seen in some Cr alloy systems at the IC SDW phase transition  $T_{IC}$ , as listed in tables 1 and 2, may be explained in the GT theory as being a consequence of  $dT_{IC}/dp$  having a positive sign in these systems.

A positive value of  $dT_{IC}/dp$  is indeed observed in two of the three systems having a continuous IC SDW phase transition at which there is a positive thermal expansion anomaly  $\Delta\beta(T)$  (namely, CrMn and CrGe), and also a negative value for both  $dT_{IC}/dp$  and  $\Delta\beta(T)$  in one system for which the IC SDW phase transition is first-order (namely, CrFe). The exceptional system, in which the continuous IC SDW phase transition has a *positive* value of  $\Delta\beta(t)$ , with a transition temperature  $T_{IC}$  that *decreases* with pressure, is CrGa. We do not understand this discrepancy with the prediction of the GT theory, and suggest that the pressure dependence of IC SDW phase transition in CrGa should be explored by neutron diffraction to see whether, instead of having a genuine continuous transition a mixed phase might exist as in CrAl (Mizuki *et al* 1982)

Even in the Cr alloy systems CrMn and CrGe, however, where the magnetic Grüneisen parameter  $\Gamma_{IC}$  obtained from  $dT_{IC}/dp$  has the same sign as  $\Gamma_{IC}$  calculated by means of the GT theory from the ratio of  $\Delta\beta(T)$  to the magnitude  $\Delta B(T)$  of the anomaly in the bulk modulus, the size of  $\Gamma_I$  and  $\Gamma_{IC}$  differ by more than one order of magnitude. This result throws into doubt the specific form of the GT theory formulated by Fawcett (1989), but not the general thermodynamic principles that relate the signs of  $dT_{IC}/dp$ ,  $\Delta\beta(T)$  and  $\Delta B(T)$ .

The pronounced anomaly in the shear modulus  $G(T)$  seen around  $T_{IC}$  in CrRu tells us that the shear strain dependence of the IC SDW phase transition is relatively large in this Cr alloy system. The maximum in the thermal expansion  $\beta(T)$  seen at this phase transition indicates that the shear strain dependence of  $T_{IC}$  is negative, i.e., the shear magnetic Grüneisen parameter is positive (see equation (8)).

In the present paper, we summarize the experimental evidence for a direct connection between the nature of the anomalies in the magnetoelastic properties of the Cr alloy systems that have been measured and the pressure dependence of their magnetic phase transitions, i.e., the form of the magnetic phase diagram in the pressure-temperature plane. A full account with documentation of the experimental data will be published shortly in a review paper on SDW antiferromagnetism in Cr alloys (Fawcett *et al* 1992). The method of analysis is first reviewed in section 2, while the experimental data listed in tables 1 and 2 are discussed in section 3.

**Table 1.** Experimental observation of anomalies in the magnetoelastic properties of Cr alloy systems at the Néel transition at temperature  $T_N$  and at the incommensurate-commensurate (IC) SDW phase transition at temperature  $T_{IC}$ , and the magnetic Grüneisen parameter  $\Gamma_N$  at  $T_N$ .

Group	Anomaly at $T_N$	Anomaly at $T_{IC}$	$\Gamma_N^{(a)}$	Reference
Thermal expansion $\beta$				
5	CrV	— <sup>(b)</sup>	-33	White <i>et al</i> (1986)
6	CrMo	—	-34	Venter <i>et al</i> (1986)
7	CrMn	$\widehat{\text{CrMn}}$ <sup>(c)</sup>	-50	Alberts and Lourens (1987) Butylenko (1989)
	CrRe	x <sup>(d)</sup>	-20	Butylenko (1985)
8	CrFe	CrFe	-50	Butylenko (1989) Hausch and Török (1977)
	CrCo	x	-30	Alberts and Lourens (1983)
	CrRu	$\widehat{\text{CrRu}}$	-80	Alberts and Lourens (1988b)
	CrOs	x	-80	Butylenko (1985)
	CrPt	$\widehat{\text{CrPt}}$		Alberts and Lourens (1988c)
3	CrAl	x	-40	Alberts and Lourens (1984a)
	CrGa	$\widehat{\text{CrGa}}$	-25	Alberts and Lourens (1985)
4	CrSi	$\widehat{\text{CrSi}}$	-45	Alberts and Lourens (1988a)
	CrGe	$\widehat{\text{CrGe}}$	-50	van Rijn <i>et al</i> (1987)
Bulk modulus $B$ or Young's modulus $Y$				
5	CrV	—		Camargo and Brotzen (1982)
6	CrMo	—		Venter <i>et al</i> (1986)
7	CrMn	CrMn		Alberts and Lourens (1987)
	CrRe(Y)	CrRe(Y) <sup>(e)</sup>		Munday (1971)
8	CrFe	CrFe		Edwards and Fritz (1974, 1975)
	CrFe(Y)	CrFe(Y)		Hausch and Török (1977)
	CrRu	CrRu		Alberts and Lourens (1988b)
	CrRu(Y)	CrRu(Y)		Munday (1971)
	CrRh(Y)	CrRh(Y)		Munday (1971)
	CrPt	CrPt		Alberts and Lourens (1988c)
3	CrAl	x		Alberts and Lourens (1984a)
	CrGa	CrGa		Alberts and Lourens (1985)
4	CrSi	x		Alberts and Lourens (1988a)
	CrGe	CrGe		van Rijn <i>et al</i> (1987)
Shear modulus $G$ <sup>(f)</sup>				
8	CrFe	CrFe(Y)		Hausch and Török (1977)
	x	CrRu		Alberts and Lourens (1988b)
4	CrSi	x		Alberts and Lourens (1988a)

(a) In case alloys of several compositions have been measured, the value of  $\Gamma_N$  for the most dilute alloy is quoted (Fäwccett *et al* 1992).

(b) CrV and CrMo are also listed for completeness, though these Cr alloy systems do not exhibit a commensurate SDW phase. The dash symbol (—) indicates accordingly that the ICSDW phase transition does not exist. To our knowledge this tabulation of elastic constant references is thus complete, but thermal expansion data exist for some other Cr alloy systems.

(c) The hat symbol ( $\widehat{\text{CrA}}$ ) indicates that the thermal expansion anomaly at  $T_{IC}$  in the CrA alloy system is a maximum.

(d) The cross symbol (x) indicates that no anomaly is observed at this transition.

(e) The notation (Y) for both the transition at  $T_N$  and that at  $T_{IC}$  indicates that a broad deep minimum was observed in the temperature dependence of the Young's modulus which, as described in the text, is interpreted as being the result of the coalescence of two unresolved minima.

(f) Cr alloy systems in which the shear modulus  $G$  was measured, but no anomaly was observed either at the Néel transition or at the ICSDW phase transition: CrCo, CrAl, CrGa and CrGe, and also the two systems CrV and CrMo that do not have a triple point.

**Table 2.** Magnetic Grüneisen parameters of Cr alloy systems  $\text{Cr}_{1-x}\text{A}_x$  at the incommensurate-commensurate (IC) SDW phase transition.  $\Gamma_{\text{IC}}$  is the volume strain and  $\Gamma_{\text{GIC}}$  the shear strain magnetic Grüneisen parameter, while  $\Gamma_1$  is obtained from the pressure dependence of  $T_{\text{IC}}$ .

Solute A	Concentration $x$ (at.%)	$\Gamma_{\text{IC}}$	$\Gamma_1$	$\Gamma_{\text{GIC}}$	Reference
Mn	0.23	?	200		(1/2) <sup>(a)</sup>
	0.33	?			
Ru	0.3	5		1	(3)
	0.5	5		3	
Pt	0.3	<5			(4)
Ga	1.4	25	-60		(5/6,7)
Ge	0.7	10	170		(8/9)

(a) The notation (1/2) means that  $\Gamma_{\text{IC}}$  is obtained from data in reference (1), and  $\Gamma_1$  from reference (2). The question mark (?) here means that  $\Gamma_{\text{IC}}$  can in principle be determined for this system, but not in practice from the data given in reference (1).

(1) Alberts and Lourens (1987).

(2) Mizuki *et al* (1982).

(3) Alberts and Lourens (1988b).

(4) Alberts and Lourens (1988c).

(5) Alberts and Lourens (1985).

(6) Kaneko *et al* (1982).

(7) Alberts and Lourens (1984b).

(8) van Rijn *et al* (1987).

(9) van Rijn and Alberts (1986).

## 2. Theory

In the GT theory (Fawcett 1989) the magnetic free energy is written in terms of general functions of reduced temperature containing volume-dependent temperature (energy) parameters that are different above and below the Néel temperature  $T_{\text{N}}$ . When we apply this theory to the IC SDW phase transition, we simplify the analysis by assuming that the magnetic free energy may be expressed in the neighbourhood of the transition in terms of a single function

$$\Delta F(t) = \phi f[t_{\text{IC}}(\omega)] \quad t_{\text{IC}}(\omega) = T/T_{\text{IC}}(\omega). \quad (1)$$

The IC SDW phase transition temperature parameter  $T_{\text{IC}}(\omega)$  is assumed to be a linear function of volume strain  $\omega$ , and to be isotropic in strain, as is implicit in assuming dependence on  $\omega$  rather than upon the individual uniaxial components of strain. We then obtain (Muir *et al* 1987, equations (2b) and (6c))

$$\Delta \beta(t) = \frac{\phi}{B(t)T_{\text{IC}}} \frac{d \ln T_{\text{IC}}}{d\omega} [f'(t) + t f''(t)] \quad (2)$$

and

$$\Delta B(t) = \phi \left( \frac{d \ln T_{\text{IC}}}{d\omega} \right)^2 t [2f'(t) + t f''(t)]. \quad (3)$$

The ratio of the anomalies in the magnetoelastic properties enables us to define a magnetic Grüneisen parameter

$$\Gamma_{\text{IC}} = - \frac{d(\ln T_{\text{IC}}(\omega))}{d\omega} = - \frac{1}{B_{\text{IC}} T_{\text{IC}}} \lim_{t \rightarrow 1} \frac{\Delta B(t)}{\Delta \beta(t)} \quad (4)$$

where we have written  $B_{IC}$  for the bulk modulus at the phase transition temperature  $T_{IC}$ , where  $t = 1$ , and have assumed the inequality

$$|f''(t)| \gg |f'(t)| \quad (5)$$

to hold at temperatures close to  $T_{IC}$ . We shall have cause to examine these assumptions again, and especially the latter, in section 3.

In the present case, equation (4) is used primarily to determine the *sign* of  $\Gamma_{IC}$ , rather than its magnitude. The sign will in fact be the same as the sign of the anomaly in the thermal expansivity

$$\Delta \beta(A) = \beta(A) - \beta(P) \quad (6a)$$

since the anomaly in the bulk modulus

$$\Delta B(A) = B(A) - B(P) \quad (6b)$$

is always negative. In equations (6), A refers to the alloy CrA and P refers to a hypothetical system, which in practice has been taken to be the paramagnetic alloy, Cr + 5 at.% V, whose thermal expansion (White *et al* 1986) and bulk modulus (Alberts 1990) are assumed to have only negligible magnetic contributions. The experimental fact that  $\Delta B(A)$  always shows minima at both  $T_N$  and  $T_{IC}$  corresponds to the assumptions made in deriving equation (4) that the function  $f(t)$  in equation (1) has a negative second derivative, as one might expect in the case of the Néel transition if its temperature dependence resembles that of an order parameter, and furthermore that the magnetic free energy in equation (1) is linear in the volume strain, and does not have any appreciable tetragonal shear strain dependence (Muir *et al* 1987). We shall discuss this result again in section 3.

We note that equation (4) corresponds to the Ehrenfest relation for a second-order phase transition at temperature  $T_i$

$$\Gamma_i = -\frac{1}{\bar{B}_i T_i} \frac{(\Delta B)_i}{(\Delta \beta)_i} \quad (7)$$

where  $(\Delta B)_i$  and  $(\Delta \beta)_i$  are the discontinuities in the magnetoelastic properties, and  $\bar{B}_i$  the average bulk modulus, at the transition. In Cr alloys the magnetoelastic properties do not however show discontinuities at the phase transitions, with the exception of the strongly first-order transitions to the commensurate SDW phase in the CrFe and CrSi systems, and possibly the IC SDW phase transition in single crystal CrRu, which may show first-order behaviour for both the shear moduli,  $c_{44}$  and  $1/2(c_{11} - c_{12})$  (Alberts and Boshoff 1992).

In the absence of discontinuities in the magnetoelastic properties at the continuous IC transitions, the magnetic Grüneisen parameter  $\Gamma_{IC}$  characterizing the transition should be evaluated, like those at the Néel transition, by analysis of the temperature dependence of their magnetic contributions by use of equation (4). We have not performed such an analysis, since the temperature intervals both above and below  $T_{IC}$ , over which  $\Delta \beta(t)$  and  $\Delta B(t)$  are linearly related, turn out to be rather small.

It is however possible to obtain a very rough estimate of  $\Gamma_{IC}$  by use of the Ehrenfest-like equation (4), with  $(\Delta B)_{IC}$  and  $(\Delta \beta)_{IC}$  being taken as the maximum deviation of each quantity from the curve for the nonmagnetic reference, which is



assumed to be asymptotic to the observed curves above and below the transition. A still lower level of analysis, which nevertheless provides the sign of the magnetic Grüneisen parameter  $\Gamma_{IC}$ , is to compare the signs of  $(\Delta B)_{IC}$  and  $(\Delta\beta)_{IC}$ . If as is usually the case they are of opposite sign, then equation (4) shows that  $\Gamma_{IC}$  is positive.

We shall compare the value of  $\Gamma_{IC}$  obtained from the magnetoelastic properties with a magnetic Grüneisen parameter

$$\Gamma_I = -\frac{d(\ln T_{IC})}{d\omega} = B_{IC} \frac{d(\ln T_{IC})}{dp} \quad (8)$$

obtained directly from the pressure dependence of  $T_{IC}$  by use of the bulk modulus  $B_{IC}$  at the IC SDW phase transition. The notation  $\Gamma_I$  follows the convention adopted by Fawcett (1989) of using a single-letter subscript for a Grüneisen parameter obtained from the pressure dependence of a transition temperature.

We turn now to the determination of the magnetic Grüneisen parameter corresponding to shear strain  $\epsilon_\alpha$  for a phase transition at temperature  $T_i$ , which, assuming again the inequality (5), may be written (Muir *et al* 1987, equation (2d)),

$$\Gamma_{GI} = -\frac{d\ln(T_i(\epsilon_\alpha))}{d\epsilon_\alpha} = -\frac{1}{B_i T_i} \lim_{t \rightarrow 1} \left( \frac{\Delta G(t)}{\Delta\beta(t)} \right) \quad (9)$$

This expression refers to pure shear strain in a single crystal, but in all cases that we shall consider the shear modulus  $G$  was obtained by measuring the transverse sound velocity in a polycrystalline sample. This modulus corresponds in fact to a combination of both longitudinal and transverse strain, and the analysis giving the expression for the corresponding Grüneisen parameter is beyond the scope of this paper. We shall proceed with the simplifying assumption that equation (9) is the expression relevant to the present discussion.

### 3. Discussion

The thermal expansion anomalies at temperatures of about 300 K and 270 K in figures 1(c) and 1(e), for Cr + 0.23 at.% Mn and Cr + 0.33 at.% Mn, respectively, serve to identify unambiguously the IC SDW phase transition temperature  $T_{IC}$  in these two alloys. In both cases, however, the corresponding anomaly in the bulk modulus is *not* apparent in figures 1(d) and 1(f). The sharp minimum seen at the Néel temperature,  $T_N \simeq 320$  K, in figure 1(b) for a  $Cr_{1-x}Mn_x$  alloy containing  $x < x_L \simeq 0.2$  at.% Mn, where  $x_L$  is the triple-point concentration (Fawcett *et al* 1992), becomes much broader however in figures 1(d) and 1(f) for the two alloys having concentrations,  $x > x_L$ . We ascribe this behavior to the coalescence of two relatively sharp minima in the temperature dependence of the bulk modulus at  $T_N$  and  $T_{IC}$ . The reason that the anomalies at  $T_N$  and  $T_{IC}$  are resolved in thermal expansion is simply that they have opposite sign.

In  $Cr_{1-x}Ru_x$ , two alloys having  $x > x_L = 0.16$  at.% Ru (Butylenko and Nev-dacha, 1980) show well resolved anomalies at both  $T_N$  and  $T_{IC}$  in the bulk modulus (figures 2(b) and 2(e)) as well as the thermal expansion (figures 2(c) and 2(d)). The data of Munday (1971) for the temperature dependence of the Young's modulus  $Y(T)$  of CrRu alloys show a sharp minimum for  $x = 0.15$  at.% Ru, essentially the

triple-point concentration, and much a deeper and broader minimum for  $x = 0.27$  at.% Ru. This is about the same concentration as that in the alloy for which the temperature dependence of the thermal expansion is shown in figure 2(b), which indicates that this broad deep minimum in  $Y(T)$  does indeed result from the coalescence of minima at  $T_N$  and  $T_{IC}$ .

Munday (1971) found similar behaviour for  $Y(T)$  in a  $Cr_{1-x}Re_x$  alloy having  $x = 0.30$  at.% Re, and in a  $Cr_{1-x}Rh_x$  alloy having  $x = 0.30$  at.% Rh, while  $Cr_{1-x}V_x$  alloys with  $x = 0.29$  and  $0.61$  at.% V showed no such broad deep minimum. Munday's data thus indicated the existence of a commensurate SDW phase and provided an upper bound for the triple-point concentration  $x_L$  in the three Cr alloy systems, CrRe, CrRu and CrRh, some ten years before the phase diagrams based on the data of Butylenko and Nevdacha (1980) for the temperature dependence of the resistivity were available. The absence of a broad deep minimum in  $Y(T)$  for CrV alloys of course corresponds to the absence of a commensurate SDW phase in this system.

The identification of the exact position of a phase transition from the anomaly in the temperature dependence of a physical property is a vexed problem. The temperature dependence of the electrical resistivity  $\rho(T)$  may show a true minimum, or merely a shoulder on the side of a curve corresponding to  $\rho$  rising rapidly with temperature  $T$ , but in either case the derivative  $d\rho/dT$  is a minimum (i.e., the inflection on the low- $T$  side of the minimum in  $\rho(T)$  or in the middle of the shoulder), and provides a better estimate of the Néel temperature  $T_N$  than the minimum in  $\rho(T)$  itself, or any other feature of the anomaly (Arajs *et al* 1973, 1980).

The physical origin of the anomalies in the thermal expansivity  $\beta(T)$  and the bulk modulus  $B(T)$  is however quite different from that of the anomaly in  $\rho(T)$ , and the choice of minimum or inflection point to identify  $T_N$  must be argued on its merits. In the first paper in the series by Alberts and coworkers (1983), it was pointed out that in CrCo alloys the minima in  $\beta(T)$  and  $B(T)$  agree better with the inflection point in  $\rho(T)$  (minimum in  $d\rho/dT$ ) than with the minimum, which gives confidence in our use of these features to identify the transition temperatures.

CrGa (Alberts and Lourens 1985) was the first Cr alloy system for which anomalies in  $\beta(T)$  and  $B(T)$  were observed at the IC SDW phase transition, and there was some difficulty in determining  $T_N$  and  $T_{IC}$  when both transitions gave rise to minima in  $B(T)$ , which coalesced to form a single broad minimum. Alberts and Lourens adopted the reasonable procedure of identifying the inflection points in  $B(T)$  on the high- $T$  and low- $T$  sides of this broad minimum (i.e., the positive and negative extrema in  $dB/dT$ ) with  $T_N$  and  $T_{IC}$ , respectively. We believe that they were mistaken, however, in adopting the same procedure for the thermal expansion  $\beta(T)$ , since when the anomaly at  $T_N$  is a minimum and that at  $T_{IC}$  a maximum, as is normally the case, it is easy and natural to define the transition temperatures by the positions of the extrema in  $\beta(T)$ .

Thus in CrMn we determine the phase transitions in this manner, as indicated in figure 1(c) and 1(e). The values of  $T_N$  obtained from the minimum in  $\beta(T)$  in figure 1(a) and the minimum in  $B(T)$  in figure 1(b) agree well, because for this low concentration,  $x = 0.09$  at.% Mn, there is only a single sharp minimum in  $B(T)$  at the Néel transition. In CrRu the minima in either  $\beta(T)$  or  $B(T)$  would serve to identify the two phase transition temperatures, since they are well separated, as is seen in figure 2.

The bulk modulus exhibits a minimum in its temperature dependence for all the

Cr alloy systems listed in table 1 at the Néel transition, and for all except CrAl and CrSi at the IC SDW phase transition (which does not exist in CrV and CrMo). Studies of the phase diagram of  $\text{Cr}_{1-x}\text{Si}_x$  under pressure, by means of neutron diffraction (Endoh *et al* 1982), show that the IC SDW phase transition is complex. In particular the incommensurate and commensurate SDW phases coexist at temperatures below about 150 K in a sample having  $x = 1.4$  at.% Si, so that  $T_{\text{IC}}$  and  $dT_{\text{IC}}/dp$  are not clearly defined.  $\text{Cr}_{1-x}\text{Al}_x$  also is still not understood, having a triple point at  $x_{\text{L}} = 1.0$  at.% Al (Fawcett *et al* 1992) while at a different concentration,  $x \gtrsim 2$  at.% Al, the magnetoelastic coupling becomes gigantic (Alberts and Burger 1978, Fawcett and Alberts 1990).

The system  $\text{Cr}_{1-x}\text{Fe}_x$  is of course exceptional in that the phase transition to the commensurate SDW phase for concentrations  $x$  both above and below the triple point,  $x_{\text{L}} = 2.4$  at.% Fe (Butylenko 1989, Fawcett and Galkin 1992) are strongly first-order. Nevertheless, the Young's modulus at both the Néel transition ( $x > x_{\text{L}}$ ) and the IC SDW phase transition ( $x < x_{\text{L}}$ ) shows a  $\lambda$ -type anomaly (Hausch and Török 1977, see figure 3) rather similar to that seen in pure Cr (Fine *et al* 1951), thus indicating a minimum in  $B(T)$  for this system also (see also figure 6 of Hausch and Török 1977).

While  $B(T)$  normally exhibits minima at both  $T_{\text{N}}$  and  $T_{\text{IC}}$ , reference to table 1 shows that the thermal expansion  $\beta(T)$  always exhibits a minimum at  $T_{\text{N}}$ , but either a maximum at  $T_{\text{IC}}$ , or no anomaly at all, with CrFe and CrSi being exceptional, as noted earlier, because of the first-order transition to the commensurate SDW phase. Thus according to equation (4), and its analogue for the Néel transition, while the sign of  $\Gamma_{\text{N}}$  is negative for all these alloys, as is normal for Cr alloy systems (Fawcett *et al* 1992), the sign of  $\Gamma_{\text{IC}}$  is positive.

If we assume, as is reasonable, that  $\Gamma_{\text{IC}}$  has the same sign as  $\Gamma_{\text{I}}$ , which is obtained from the pressure dependence of the IC SDW phase transition temperature  $T_{\text{IC}}$ , according to equation (8), the results listed in table 1 predict that  $dT_{\text{IC}}/dp$  will be positive for all these Cr alloys systems. This prediction is confirmed in CrMn (Mizuki *et al* 1982) and CrGe (van Rijn and Alberts 1986), while the pressure-temperature phase diagram has not been measured for CrRu and CrPt. In CrSi the IC SDW phase boundary, as determined by neutron diffraction measurements under pressure (Endoh *et al* 1982), is poorly defined, so that  $dT_{\text{IC}}/dp$  cannot be determined.

The system  $\text{Cr}_{1-x}\text{Fe}_x$  is worth special consideration. The thermal expansion data of Hausch and Török (1977, see figure 1) show two phase transitions in samples containing  $x = 1.95, 2.6$  and  $3.8$  at.% Fe, the upper temperature one being continuous and the lower first-order. The latter is clearly the IC SDW phase transition, though the appearance of an anomaly at a higher temperature is puzzling for the samples containing  $x = 2.6$  and  $3.8$  at.% Fe, since the triple-point concentration is  $x_{\text{L}} = 2.4$  at.% Fe (Butylenko, 1989). Similar behaviour is seen however in CrRe and CrOs (Butylenko 1985), where a weak anomaly occurs some 50–100 K above the continuous Néel transition to the commensurate SDW phase. The thermal expansivity  $\beta$  below and above the IC SDW phase transition is about  $3$  and  $8 \times 10^{-6} \text{ K}^{-1}$ , respectively. Thus, even though the phase transition is first-order, the change in  $\beta$  at the transition corresponds to a minimum in  $\beta$ . This behaviour is analogous to that seen in pure Cr, where there is a weak first-order Néel transition, but also a clear minimum in  $\beta$  at  $T_{\text{N}}$  (White *et al* 1986).

The minimum in  $\beta$  at  $T_{\text{N}}$  leads us to expect, according to equation (4), a positive pressure dependence of  $T_{\text{IC}}$  in CrFe, which is in fact observed (Mizuki *et al*, 1982).

The reason that CrFe is exceptional in having an IC SDW phase transition temperature that increases with pressure is clear from an examination of figure 9 of Mizuki *et al* (1982). The CrFe system is anomalous in having the line of IC phase transitions lying beneath the incommensurate SDW phase in the composition-temperature phase diagram (Ishikawa *et al* 1967). Nakanishi and Kasuya (1977) have related the strong magnetovolume changes seen at the phase transitions in CrFe to the unusual form of the composition-temperature phase diagram.

The pressure-composition phase diagram is likewise anomalous (Edwards and Fritz 1974, 1975), following the general pattern, whose explanation is still not understood (Fawcett *et al* 1992), that in Cr alloy systems the effect of pressure is analogous to decreasing electron concentration, with impurity atoms of groups 7 and 8 contributing electrons and therefore producing effects similar to negative pressure.

Another remarkable feature of the CrFe system is an apparent reentrant commensurate SDW phase seen in the ternary alloy system,  $(\text{Cr} + x \text{ at.}\% \text{ Fe})_{1-x} (\text{V,Mn})_x$ . For some compositions three phase transitions are seen with decreasing temperature, the Néel transition to the incommensurate SDW phase and then the IC SDW phase transition, both giving a minimum in the thermal expansivity  $\beta(T)$ , followed by a transition giving a maximum in  $\beta(T)$  to a new phase of unknown nature (Fawcett and Galkin 1992).

The  $\text{Cr}_{1-x}\text{Ga}_x$  system also has an anomalous pressure-temperature phase diagram in that  $dT_{\text{IC}}/dp$  is negative (Kaneko *et al* 1982, Alberts and Lourens 1984b), but in this case the thermal expansion has a maximum at  $T_{\text{IC}}$  (Alberts and Lourens 1985). Thus  $\Gamma_{\text{IC}}$  and  $\Gamma_{\text{I}}$  calculated by means of equations (4) and (8), respectively, have opposite signs, as seen in table 2. We do not understand this result, but note that the behaviour of the IC SDW phase transition under pressure in CrGa is rather peculiar. Thus Alberts and Lourens (1984b) found the anomaly in the temperature dependence of the resistivity  $\rho(T)$  signalling the IC SDW phase transition to be absent in a sample containing,  $x = 0.92$  at.% Ga, while it appeared distinctively in this alloy on the application of hydrostatic pressure. At atmospheric pressure an anomaly at  $T_{\text{IC}}$  was found in  $\rho(T)$  for samples containing,  $x = 0.73$  and 1.18 at.% Ga, but not for alloys containing,  $x \gtrsim 1.2$  at.% Ga.

Booth *et al* (1983) studied the phase diagram of  $\text{Cr}_{1-x}\text{Ga}_x$  using alloys containing  $x = 0.5, 0.75, 1.0, 3.0$  and higher at.% Ga, and found no evidence of a triple point, since all alloys showed a commensurate SDW phase over some temperature interval between the incommensurate SDW phase and the paramagnetic phase. Perhaps the explanation for the anomalous behaviour of CrGa is that the IC SDW phase transition has some peculiarity like coexistence of the two phases. Further study of this system is recommended.

An alternative explanation that throws doubt on the application of the GT analysis to the IC SDW phase transition may also explain the large discrepancy in the magnitudes of  $\Gamma_{\text{IC}}$  and  $\Gamma_{\text{I}}$  in the systems CrMn and CrGa (see table 2). It may be that the function  $f(t)$  in equation (1) does not satisfy the inequality (5), and although  $f'(t) < 0$ , since  $f(t)$  vanishes at  $t = 1$ , we do not know the sign of  $f''(t)$ . In this case the ratio  $\Delta B(t)/\Delta\beta(T)$  would not provide the magnetic Grüneisen parameter as in equation (4), but a quantity whose sign even is indeterminate.

One might even speculate that the functional form of equation (1) is inappropriate for the IC SDW phase transition, and perhaps the prefactor  $\phi(\omega)$  should be a function of volume strain rather than the reduced temperature  $t_{\text{IC}}$ . In this case, however, there would be no reason for the positive sign of the anomaly in  $\beta(T)$  being normal

at this transition, which the GT theory relates to the fact that  $T_{IC}$  normally increases under pressure. Thus we regard the GT theory as providing a qualitative, but only a semi-quantitative, understanding of the magnetoelastic properties of the IC SDW phase transition.

Finally we consider the behaviour of CrRu, which is a unique Cr alloy system in that it shows a large anomaly in the temperature dependence of the shear modulus, as illustrated in figure 2. The data for the Cr + 5 at.% V alloy serve well as the non-magnetic reference, which enables us to estimate by subtraction, according to equation (6a), the magnetic contribution  $\Delta\beta(T)$  to the thermal expansion at the IC SDW phase transition temperature  $T_{IC}$ .

In the case of the magnetic contribution  $\Delta B(T)$  to the bulk modulus, however, the decrease towards the deep minimum at the Néel temperature  $T_N$  begins at a temperature below  $T_{IC}$ , and the dot curves sketched in figures 2(b) and 2(e) show our estimate for this decrease. This curve and *not* that for the non-magnetic reference material Cr + 5 at.% V is clearly the appropriate reference for  $B(P)$  to use in equation (6b) for estimating  $\Delta B(T)$ . The corresponding values of  $\Gamma_{IC}$  obtained by use of equation (4) are given in table 2. There are no measurements under pressure with which to estimate  $\Gamma_I$  for comparison.

The dot curves showing  $\Delta G(T)$  in panels (c) and (f) of figure 2 were estimated by use of the data for Cr + 5 at.% V displaced vertically so as to be asymptotic in each case to the continuous curve  $G(T)$  at lower temperature. The maximum value of  $\Delta G(T)$ , obtained by subtraction of the two curves, occurs at a temperature some 40 K higher than the value of  $T_{IC}$  estimated from the peak in  $\beta(T)$  shown in figures 2(a) and 2(d). The ratio of these maximum values nevertheless seems to serve best to estimate roughly the shear magnetic Grüneisen parameter  $\Gamma_{GIC}$  by substitution in equation (9).

The resultant values of  $\Gamma_{GIC}$  given in table 2 are of order unity, being somewhat less but comparable in magnitude to the value of  $\Gamma_{IC}$ . There is of course no reason why one would expect the two magnetic Grüneisen parameters to be comparable in magnitude, or even to have the same sign. Indeed in other Cr alloy systems, with the exception of CrFe, we find the condition,  $\Gamma_{GIC} \ll \Gamma_{IC}$  (and  $\Gamma_{GN} \ll \Gamma_N$ ), so that anomalies are not seen at all in the shear modulus at either of the two phase transitions.

Measurements by Alberts and Boshoff (1992) on a single crystal sample of Cr + 0.3 at.% Ru give a remarkably sharp change, perhaps a first-order step in the elastic moduli, and especially in the shear moduli, as noted above, at the IC SDW phase transition. The estimates of  $\Gamma_{IC}$  and  $\Gamma_{GIC}$  obtained from the single crystal data by substituting the values of the step changes in equations (4) and (9) are however roughly the same as those for the polycrystalline sample given in table 2.

We have not attempted to estimate  $\Gamma_{NT}$  or  $\Gamma_{SF}$  below and above the Néel temperature  $T_N$  by use of equation (4), since we judge the thermal expansion data shown in figures 2(a) and 2(d) to be unsatisfactory for this purpose. Indeed, for the Cr + 0.5 at.% Ru sample, the temperature,  $T_N = 440$  K, of the transition is beyond the range of the thermal expansion equipment.

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