Magnetovolume in chromium

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The thermal-expansion data of White, Roberts, and Fawcett for Cr and antiferromagnetic Cr*V* alloys measured relative to paramagnetic $Cr_{95}V_5$ up to temperature 700 K are analyzed. The magnetovolume in the ordered state is found to be proportional to the mean-square magnetic moment and their ratio, being proportional to the magnetoelastic coupling, is discussed in relation to the predictions of a theoretical model. Explanations suggested to account for the experimental magnetovolume being somewhat smaller than theoretical estimates include volume dependence of the exchange interaction. Grüneisen parameters associated with magnetic ordering are evaluated and their large values are contrasted with the normal value of order unity obtained by comparing the thermal expansion with the specific heat in the paramagnetic state at temperatures up to 1500 K. The magnetovolume in the paramagnetic state is compared with the mean-square moment obtained from inelastic neutron scattering.

I. INTRODUCTION

As a prototype itinerant antiferromagnet, chromium is of great fundamental interest. Accordingly, there is an extensive literature on the physical properties of chromium and its dilute antiferromagnetic alloys. In particular, elastic neutron scattering has given us a clear picture of the magnetic structure of chromium: the paramagnetic metal undergoes a first-order transition at the Néel temperature, $T_N = 311$ K, to an incommensurate transverse spin-density-wave state (the transverse SDW phase) which becomes longitudinal (the longitudinal SDW phase) at the spin-flip temperature, $T_{SF} = 123$ K (see, e.g., Werner, Arrott, and Kendrick).[1]

Overhauser[2] first realized that this incommensurate structure corresponds to a spin-density wave produced by exchange interaction between electrons at the Fermi surface. Lomer[3] showed how the Fermi surface of chromium nests so as to produce a SDW with a wave vector **Q** of about the observed magnitude and oriented along a cube axis. Two-band models[4] based on these ideas were developed to account for many of the observed magnetic properties of chromium and its dilute alloys,[5] including the magnitude and variation with temperature and alloy concentration of the wave vector **Q**, the amplitude of the SDW, and the ordering temperature.

The magnetic excitations in chromium are much less understood theoretically, but a clear experimental picture is now emerging.[6,7] The feature of perhaps greatest interest is the "commensurate-diffuse" scattering in the terminology of Grier, Shirane, and Werner,[7] which is centered on the commensurate antiferromagnetic $\{001\}$ points in reciprocal space.

Theoretical discussions[8] based on two-band models have focused interest on spin waves having high velocities related to that of electrons at the Fermi surface, which have been observed[9] in Cr*Mn* alloys having a simple commensurate SDW phase. These theories do not, however, explain the low-energy excitations responsible for the commensurate-diffuse scattering persisting to high temperatures, which is characteristic of the incommensurate SDW phase of pure chromium, and little progress has been made towards providing a satisfactory explanation of these effects.[10,11]

In a situation where theoretical models provide little or no guidance to the interpretation of detailed spectroscopic data such as that provided by neutron scattering, it is often rewarding to resort to studies of the fundamental thermophysical quantities, specific heat and thermal expansion. In the case of chromium the effect of antiferromagnetism on the specific heat is seen clearly at low temperatures. Heiniger[12] showed that the Sommerfeld coefficient Γ of the electronic term linear in temperature was reduced in antiferromagnetic alloys of chromium with respect to other transition metals. Interpolation between the nonmagnetic alloys indicates a reduction of Γ by as much as a factor two in pure chromium, with the depression of Γ in the alloys matching nicely the curve showing the concentration dependence of the Néel temperature.

Apart from this low-temperature effect, the effect of magnetism on the specific heat of chromium is small, and is seen only in careful measurements close to the phase transitions.[13,14] Indeed, the small size of the latent heat at the Néel transition was offered by Overhauser[2] as evidence for the itinerant nature of the magnetism in chromium. On the other hand, the marked dependence of the magnetic properties of chromium on elastic strain, which, as we shall see, results in a large ground-state magnetovolume and other magnetic effects in the thermal expansion, has long been known.[15]

In the present work we shall analyze the experimental data for the thermal expansion of chromium and dilute CrV alloys over the temperature range 1.5–700 K described by White, Roberts, and Fawcett.[16] Although we shall not be concerned here with anisotropic effects, we should take note also of the thermal expansion work[17–19] on single-**Q** chromium which shows that the anisotropy of the thermal expansion is small. We shall, in any case, be using only data taken with polycrystalline or single-crystal (but still multidomain) samples, so that we can ignore anisotropic effects when deriving the magnetovolume from linear thermal expansion data. We shall not be concerned here particularly with the thermal expansion below 100 K, which was treated by Kaiser, White, and Fawcett.[19]

The importance of magnetovolume effects in magnetic metals has long been recognized, the most intensively studied and the most important technically being the Invar alloys.[20] Holden, Heine, and Samson[21] developed a model to consider the thermal expansion of transition metals, which they applied to Fe, Ni, and Cr. They showed that the magnetic pressure and hence, with a temperature-independent bulk modulus, the magnetovolume, may be expressed as a function of temperature T up to and beyond the ordering temperature in terms of the mean-square magnetic moment $\langle M^2(T)\rangle$, the exchange interaction parameter I, and the volume dependence of the density of states in the d band.

We shall use the formulation of this model given by Kaiser and Haines[22] in which I is assumed also to be volume dependent. They obtain, for the magnetovolume in chromium,

$$\omega_M(T)=\frac{V(T)-V_0}{V_0}=\frac{C}{B_0}\langle M^2(T)\rangle,\quad C=\beta_1\frac{(1-\beta_2)I}{4V_0} \tag{1}$$

by neglecting the weak temperature dependence of the magnetic part of the internal energy and by using, like Holden, Heine, and Samson,[21] the zero-temperature value B_0 of the bulk modulus at atomic volume V_0. In Eq. (1) the parameters β_1 and $-\beta_1\beta_2$ are, respectively, the volume dependencies of the density of states N at the Fermi surface and of the exchange interaction parameter I,

$$\beta_1=\frac{d\ln N}{d\omega},\quad -\beta_1\beta_2=\frac{d\ln I}{d\omega}\ . \tag{2}$$

Holden, Heine, and Samson[21] adopted the values, $\beta_1=5/3$, $\beta_2=0$, thus obtaining

$$\frac{\omega_M(T)}{\langle M^2(T)\rangle}=\frac{C}{B_0}=\frac{5}{12}\frac{I}{B_0V_0}\quad\text{or } C=\frac{5I}{12V_0}\ . \tag{3}$$

It should be pointed out that the relation (1) between the magnetovolume and the mean-square magnetic moment for the case of ordered moments goes back a long way in the history of ferromagnetism.[23] Wohlfarth[24] discussed earlier work in the context of magnetostriction of ferromagnetic metals. We note that, for an incommensurate SDW system like chromium, $\langle M^2\rangle$ is obtained by spatial as well as thermal averaging of the magnitude of the moment $\mathbf{M}(\mathbf{r},T)$. Thus at zero temperature, a sinusoidal SDW of amplitude M_0 gives $\langle M^2\rangle=\frac{1}{2}M_0^2$.

In the experimental studies of White, Roberts, and Fawcett[16] the magnetic contribution to the thermal expansivity of chromium was separated out from the total by comparing pure chromium with a dilute paramagnetic alloy of chromium with another metal. Vanadium was chosen since the addition of small amounts of V to Cr quickly reduces T_N and no magnetic ordering occurs for a V concentration above about at. 4%.[5] Thus a comparison of pure Cr with the paramagnetic alloy $Cr_{95}V_5$ will provide a measure of the effects associated with magnetic order in the thermal expansion of Cr. A comparison of the dilute antiferromagnetic alloys $Cr_{100-x}V_x$ for $x<4$ at. % with $Cr_{95}V_5$ provides another experimental parameter, the concentration x of V, by means of which the Néel temperature can be progressively depressed and the magnetic effects turned off.

This method may fail to separate out one magnetic effect, namely the spin fluctuations predicted by Moriya,[25] since it is suggested that these can occur in a transition metal or alloy which does not exhibit any long-range magnetic order. Spin fluctuations have associated magnetovolume[26] and their amplitude increases with temperature, so that at high temperatures, well above T_N, we might expect their effect on the thermal expansion to be very similar in $Cr_{95}V_5$ and in pure Cr. Thus the differential method may be unable to reveal such effects.

The plan of the paper is as follows. We first, in Sec. II, define rather carefully the physical quantities "magnetovolume" and "magnetic thermal expansivity." In Sec. III, where we consider the thermal expansion in the ordered state, we discuss some anomalous features of neutron diffraction data which should be taken into account when a comparison is made between the temperature dependence of the magnetovolume $\omega_M(T)$ in the ordered state with $\langle M^2(T)\rangle$ determined from the intensity of the magnetic satellites.

We proceed, in Sec. IV, to analyze the thermal expansion in chromium around its Néel temperature T_N. Comparison with the specific-heat data of Williams, Gopal, and Street[14] gives large negative values for the Grüneisen parameter, as does the pressure dependence of T_N itself. We discuss in Sec. V the remarkable change in the nature of the Néel transition when chromium is diluted by as little as 0.5 at. % V: although the Néel temperature is depressed by only about 15%, the clearly first-order transition in pure Cr becomes an apparently continuous transition in $Cr_{99.5}V_{0.5}$.

In Sec. VI we discuss in some detail the recent work on inelastic neutron scattering in chromium as it relates to the high-temperature thermal expansion of chromium and CrV alloys in the paramagnetic phase. We assemble the several magnetic Grüneisen parameters in Table I and discuss the significance of the fact that they are all large while the overall Grüneisen parameter at high temperatures above about 500 K is small. In Sec. VII we discuss the magnitude of the ground-state magnetovolume that we have deduced in Cr and antiferromagnetic Cr*V* alloys in comparison with theoretical estimates. We attempt to explain the fact that the experimental value of the ground-state magnetovolume is about three times smaller than the value predicted by the theory of Holden, Heine, and Samson.[21] We complete the paper with our conclusions in Sec. VIII.

II. DEFINITION OF MAGNETOVOLUME AND MAGNETIC THERMAL EXPANSIVITY

We have referred in Sec. I to a magnetovolume $\omega_M(T)$, which was defined as a theoretical quantity in Eq. (1). We now wish to define a corresponding experimental quantity, for which we shall use the same notation since the context will make it clear to which we are referring. Some care is necessary in making a precise definition since, as seen in Eq. (1), $\omega_M(T)$ is a fractional volume *change*, which can be defined operationally in a magnetic material only if we can compare it with the nonmagnetic state of a fiducial material which otherwise has essentially the same properties.

In the case of chromium and dilute antiferromagnetic alloys Cr*V* we use as reference material the paramagnetic alloy $Cr_{95}V_5$. We define the magnetovolume $\omega_M^A(T)$ for an antiferromagnetic alloy *A* by use of the equations

$$\omega_M^A(T)=\Delta\omega_A(T)-\Delta\omega_P(T)=\frac{\Delta V_A(T)-\Delta V_P(T)}{V_0}\ , \qquad (4)$$

with

$$\frac{\Delta V_{A(P)}(T)}{V_0}=3\int_{T_h}^{T}\alpha_{A(P)}(T)dT\ . \qquad (5)$$

The reference temperature T_h is chosen to be sufficiently high that the thermal expansivities $\alpha(T)$ of pure Cr, $\alpha_A(T)$ of the antiferromagnetic alloys, and $\alpha_P(T)$ of the paramagnetic alloy $Cr_{95}V_5$ are all equal for $T\geq T_h$. The highest temperature 700 K in the measurements of White, Roberts, and Fawcett[16] is sufficiently high to be a suitable choice for T_h, since the three curves showing the thermal expansivities of pure Cr, $Cr_{99.5}V_{0.5}$, and $Cr_{95}V_5$ all converge at least 100 K below this temperature. Because the expansivities are all equal, it is likely that the contribution of spin fluctuations or of disordered local moments to the volume is the same in these three samples even at T_h.[22] The observation[16] of a similar convergence for Cr*V* alloys with 1.5, 2.5, and 3.4 at. % V reinforces this conclusion. The only other possibility is a temperature-independent additional moment in the ordered systems well above the ordering temperature.

We show in Fig. 1 the magnetic thermal expansivity $\alpha_M(T)$ of chromium determined from the data of White, Roberts, and Fawcett[16] and $\alpha_M^{0.5}(T)$ defined in a way similar to the definition of $\omega_M^A(T)$ in Eq. (4):

$$\alpha_M^A(T)=\alpha_A(T)-\alpha_P(T)\ . \qquad (6)$$

III. THERMAL EXPANSION IN THE ORDERED STATE

We have in Eq. (1) a relation between the magnetovolume $\omega_M(T)$ of chromium and the spatial and thermal

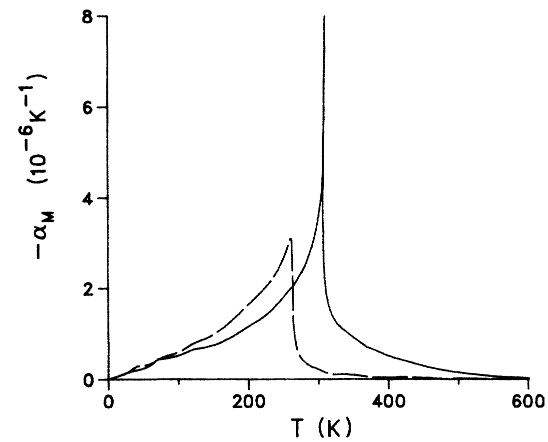

FIG. 1. Temperature dependence of the magnetic thermal expansivity α_M in chromium (——) and $\alpha_M^{0.5}$ in the antiferromagnetic alloy $Cr_{99.5}V_{0.5}$ (— — —) measured relative to the paramagnetic alloy $Cr_{95}V_5$.

average of the square of its magnetic moment $\langle M^2(T)\rangle$. The spatial average of the ordered moment can be determined from the intensity of elastic neutron scattering (neutron diffraction) at the magnetic reciprocal-lattice points. Kaiser[27] first pointed out that, in the case of chromium, the decrease of neutron diffraction intensity and therefore $\langle M^2(T)\rangle$ with increasing temperature T throughout the ordered state[1] parallels roughly the temperature dependence of the magnetovolume.[16]

This behavior, which is illustrated in Fig. 3, tells us that the magnetoelastic coupling constant C is indeed constant and positive as we expect from Eq. (3). We shall obtain the value of C when we come, in Sec. VII, to compare the change in magnetovolume with the change in the mean-square magnetic moment of chromium determined from neutron diffraction experiments.

We note, however, that a closer examination of the neutron diffraction data of Werner, Arrott, and Kendrick[1] reveals two features that appear to be at variance with Eq. (3). The first is the apparent discontinuity in the intensity at the spin-flip transition at temperature $T_{SF}\simeq 123$ K (see Fig. 2 of Ref. 1). This occurs because, in the transition from a longitudinal SDW to a transverse SDW, the distribution of intensity changes between the different magnetic satellites, depending as it does upon the relative directions of the neutron scattering vector and the SDW polarization direction, i.e., the direction of the moment. Since the extinction due to multiple Bragg scattering is different for each magnetic satellite, it is difficult to tell from neutron diffraction data whether there is a real discontinuity in $\langle M^2(T)\rangle$.

The discontinuity in volume at T_{SF} is[17]

$$\delta\omega(T_{SF})=\omega(T_{SF+})-\omega(T_{SF-})=-1.4\times10^{-6}\ , \qquad (7)$$

while the ground-state magnetovolume is $\omega_M(0)\simeq 1.4\times10^{-3}$ (see Fig. 3). We can use this information in Eq. (3) to estimate the fractional change $\delta\langle M^2(T_{SF})\rangle$ relative to $\langle M_0^2\rangle$ and hence the relative change $\delta\mathcal{I}$ in the neutron scattering intensity at T_{SF}

$$\frac{\delta \mathscr{I}}{\mathscr{I}_0} = \frac{\delta \langle M^2 \rangle}{\langle M_0^2 \rangle} = \frac{\delta \omega}{\omega_M(0)} \simeq -0.1\% \ . \tag{8}$$

This is very much smaller and of opposite sign to the *apparent* discontinuity in the intensity of about 10% obtained directly from the neutron scattering data.

The other feature of the neutron diffraction data in Fig. 2 of Werner, Arrott, and Kendrick,[1] which appears to disagree with the behavior expected from our thermal expansion results, is the apparent *linear* variation with temperature T of the intensity at low temperatures. Kaiser, White, and Fawcett[19] pointed out, on the other hand, that Eq. (3), in light of the third law of thermodynamics, requires a *quadratic* temperature dependence.

We suggest tentatively that the observed, roughly linear temperature dependence of the neutron diffraction intensity, may be connected with the temperature variation of "domains" of the longitudinal SDW phase, resulting in temperature-dependent extinction effects in the neutron diffraction. The existence of such domains seems likely in view of the observation at low temperatures of hysteresis of the pressure dependence of the Fermi surface[28] and also hysteresis in the magnetostriction.[29]

The thermal expansion of a series of antiferromagnetic CrV alloys[16] provided good evidence to support the proportionality between the ground-state magnetovolume $\omega_A(0)$ [$\omega_0(x)$ in the notation of Ref. 19] and the square of the Néel temperature, which had been found[5] to be approximately proportional to the low-temperature mean-square magnetic moment. The large magnitude of this linear thermal expansivity (and its sign) relative to the corresponding specific heat shows that γ_{LT} (γ_e in Table III of Ref. 16), the average low-temperature (LT) Grüneisen parameter, is large and negative, $\gamma_{LT} \simeq -10$.

IV. THERMAL EXPANSION AROUND THE NÉEL TRANSITION

When we compare the thermal expansion results of White, Roberts, and Fawcett[16] for chromium and the alloy $Cr_{99.5}V_{0.5}$ with the corresponding results of Williams, Gopal, and Street[14] for the specific heat (Fig. 2), we note first that the thermal expansivity anomalies are much larger than the specific heat anomalies near the Néel transition. This indicates at once the strong volume dependence of the magnetic effects responsible for the anomalies. We shall proceed to express the volume dependence in terms of magnetic Grüneisen parameters, postponing until Sec. V a discussion of the singular behavior at the first-order transition itself.

We shall first consider the behavior in Cr above T_N. The specific heat of $Cr_{95}V_5$ was measured by Schröder and Shable,[30] but we shall use $Cr_{99.5}V_{0.5}$ as reference material since the data of Williams, Gopal, and Street[14] for this alloy are more accurate. $Cr_{99.5}V_{0.5}$ is effectively a paramagnetic reference material in the temperature region, $T > T_N$. This may be seen in Fig. 1, where the magnetic contribution $\alpha_M^{0.5}(T_N)$ to the expansivity of this sample at $T_N = 311$ K has decreased to less than 10% of its value at $T_N^{0.5} = 263$ K.

Williams, Gopal, and Street[14] found that the specific heat of chromium coincides within an experimental accuracy of 0.2% with that of $Cr_{99.5}V_{0.5}$ (using the same sample as was used by White, Roberts, and Fawcett[16]) at all temperatures T above 313 K up to the limit of their measurements, $T \simeq 360$ K, as shown in Fig. 2. Thus the upper limit for the magnetic contribution to the specific heat in this temperature interval is $C_M \leq 2C \times 10^{-3} = 0.05$ J mol^{-1} K^{-1}, with the specific heat per unit volume of Cr being $C = 23.3$ J mol^{-1} K^{-1}. Inspection of Fig. 1 shows that the corresponding magnetic thermal expansivity difference α_M between Cr and $Cr_{95}V_5$ over the same interval varies between about -1.5×10^{-6} and -0.8×10^{-6} K^{-1}. Thus adopting an average value for the volume thermal expansivity,

$$\beta_M = 3\alpha_M = -3.5 \times 10^{-6} \ \mathrm{K}^{-1} \ , \tag{9}$$

we arrive at an estimate for the lower limit of the magnitude of the corresponding Grüneisen parameter close to and above the Néel temperature T_N (TN +),

$$|\gamma_{TN+}| = \left| \frac{\beta_M B_0}{C_M} \right| \geq 100 \ . \tag{10}$$

The sign of γ_{TN+} is negative since β_M is negative and C_M, although too small to be measured, is necessarily positive (as of course is B_0).

This Grüneisen parameter γ_{TN+} has been defined in a temperature region immediately above the Néel transition where one might expect to see effects due to critical fluctuations. We believe that our chromium sample is of sufficiently good quality that its behavior reflects the intrinsic properties of chromium. However, we must keep in mind the possibility that other physical processes associated with low-energy excitation of the incommensurate SDW continue beyond the Néel transition so that γ_{TN+} is

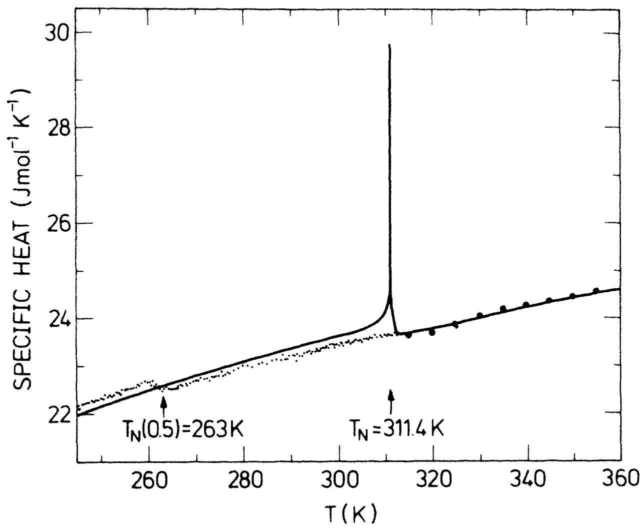

FIG. 2. Temperature dependence of the specific heat of chromium (——) and the antiferromagnetic alloy $Cr_{99.5}V_{0.5}$ (experimental data points), after Williams *et al.* with additional data supplied by Dr. I. S. Williams.

not necessarily characteristic solely of critical fluctuations.

Below the Néel transition, $Cr_{99.5}V_{0.5}$ becomes less satisfactory as a paramagnetic reference material, since with decreasing temperature it progressively develops its own magnetic thermal expansivity. However at a temperature of about 300 K, it may be seen in Fig. 1 that $\alpha_M^{0.5}$ is still much less than α_M for Cr, so that we can roughly estimate a value, $\beta_M = 3\alpha_M \simeq -10\times10^{-6}$ K^{-1}, to compare with the magnetic specific heat, $C_M \simeq 23$ mJ cm^{-3}, obtained from the data shown in Fig. 2. The resultant value of the Grüneisen parameter is $\gamma_{TN-} = -75\pm25$.

We note that γ_{TN-} characterizes the region of temperature where long-range magnetic order in chromium is decreasing rapidly as the Néel transition is approached due to physical processes which are only poorly understood. Burke, Stirling, Ziebeck, and Booth[6] believe that magnetovibrational modes of excitation are involved, while Grier, Shirane, and Werner[7] do not propose any specific model to explain the quasielastic neutron scattering which they have shown to develop in the transverse SDW phase at the commensurate point in reciprocal space and to overwhelm the elastic scattering due to long-range order as the Néel transition is approached.

The Néel temperature T_N of Cr is depressed rapidly with pressure P, the initial pressure dependence being $dT_N/dP = -51$ K/GPa.[31] McWhan and Rice[32] found that pressures up to 8 GPa depress T_N down to 84 K and that in this range $T_N(V)$ varies exponentially with volume if the bulk modulus B is assumed to be constant. In fact, B changes rapidly with temperature in the neighborhood of T_N, and is likely to change with the roughly 5% decrease in volume produced by the highest pressure, so that the exponential variation over such a wide range is to some extent fortuitous. In any case, the initial pressure dependence, with $B = 160$ GPa at T_N under ambient pressure (see Fig. 5 of Ref. 16), gives $d\ln T_N/d\ln V = 26.5$ which provides an effective measure of the magnitude of the Grüneisen parameter γ_{TN} at the Néel temperature of pure Cr.

The pressure dependence of the Néel temperature T_N^A for two Cr*V* alloys having compositions $Cr_{98.8}V_{1.2}$ and $Cr_{97.2}V_{2.8}$ has also been measured,[33] with $d\ln T_N^A/d\ln V = 26$ and 28, respectively. Thus $\gamma_{TN} = -27$ is an average value for Cr and Cr*V* alloys.

This Grüneisen parameter and the others defined in Secs. III and IV are collected in Table I. For comparison, we also give in Table I a high-temperature Grüneisen parameter, defined by use of the specific heat C_p,

$$\gamma_{HT} = \frac{3\alpha B_0}{C_p}, \tag{11}$$

which White, Roberts, and Fawcett[16] found to be essentially constant from about 500 to 1600 K.

V. THE NÉEL TRANSITION

White, Roberts, and Fawcett[16] found the Néel transition of their Cr sample to be first order, as illustrated in Fig. 3(a) of this reference. This is seen more clearly in a plot over a wider range about T_N with better temperature resolution.[34] There was no observable hysteresis within about 20 mK on cycling the temperature several times through the transition. The strain at the transition, estimated[34] by extrapolating the data above and below T_N to intersect a constant temperature line at the midpoint, $T_N = 311.0$ K, of the transition, is $\Delta l/l \le 11\times10^{-6}$, corresponding to a decrease in the magnetovolume, $\Delta\omega_M \le 33\times10^{-6}$, with increasing temperature. This is an upper limit on the value of $\Delta\omega_M$ since it undoubtedly contains below T_N some of the decrease in length associated with the continuously decreasing amplitude of the SDW, which is the order parameter in antiferromagnetic Cr and Cr*V* alloys. A lower limit is obtained by taking the interval between the extrema of $\alpha(T)$ in Fig. 3(a) of Ref. 16, $\Delta l/l \ge 8\times10^{-6}$ or $\Delta\omega_M \ge 24\times10^{-6}$. We shall adopt a value, $\Delta l/l = (10\pm1)\times10^{-6}$, closer to the maximum, which gives $\Delta\omega_M = (30\pm3)\times10^{-6}$.

Combining this with the pressure dependence of T_N (Ref. 31) in the Clausius-Clapeyron equation, we obtain a value

$$L = T\Delta\omega V_0 \frac{dP}{dT_N} = 1.3\pm0.1 \text{ J mol}^{-1} \tag{12}$$

for the latent heat L which agrees quite well with an average of the calorimetric values, $L = 1.1$ J mol^{-1}, obtained by Benediktsson, Åstrom, and Rao[35] for increasing and decreasing temperature for single crystal and polycrystal samples of Cr, and $L = 1.4$ J mol^{-1}, obtained by Williams, Gopal, and Street[14] by integrating under the specific-heat anomaly at T_N shown in Fig. 2.

The thermal expansion at the Néel transition in $Cr_{99.5}V_{0.5}$ is very different from that in pure Cr (see Fig. 3 of Ref. 16). The behavior in dilute alloys having still smaller concentrations of V suggest that, as V is introduced into Cr, the line of first-order transitions terminates in a tricritical point between 0.1 and 0.2 at % V, the Néel transition being continuous for higher concentrations.[34]

TABLE I. Grüneisen parameters in chromium and in antiferromagnetic Cr*V* alloys.

Physical process and temperature region	Grüneisen parameter
Electronic/magnetic excitations at low temperatures	$\gamma_{LT} \sim -10$
Destruction of magnetic order below T_N	$\gamma_{TN-} \sim -75$
Pressure dependence of T_N	$\gamma_{TN} \sim -27$
Critical fluctuations above T_N	$\gamma_{TN+} < -100$
Excitations in the paramagnetic phase up to $\sim 5T_N$	$\gamma_{HT} \sim 1.5$

VI. THERMAL EXPANSION AND NEUTRON SCATTERING IN THE PARAMAGNETIC STATE

The most striking feature of the magnetic thermal expansivity of chromium is perhaps its persistence for at least 200 K above the Néel temperature, as illustrated in Fig. 1. Today this behavior is not thought to be remarkable, since we have become accustomed to seeing persistence of magnetic neutron scattering in ferromagnetic metals far into the paramagnetic state.

Early neutron diffraction measurements[36] on a strain-annealed single crystal of chromium had shown magnetic scattering at the commensurate {100} points in reciprocal space at temperatures up to about 500 K. In light of recent work[7,37] it is evident that this was caused by quasielastic scattering, observed because of the absence of energy resolution in the early work.

It is important to make a clear distinction between this commensurate-diffuse scattering, which Grier, Shirane, and Werner[7] found to correspond, at all temperatures up to 500 K in the paramagnetic state, to magnetic correlations over a roughly isotropic region of dimensions about 30 Å; and paramagnetic scattering, which usually refers to scattering by disordered local spins and therefore corresponds to a correlation length of about 3 Å. To avoid confusion we shall refer to the latter as "paramagnetic-diffuse" scattering, since such a short correlation length corresponds to a diffusive mode of excitation having a wavelength comparable to or less than the correlation length.

Grier, Shirane, and Werner[7] made a systematic study of inelastic scattering in chromium through and above the Néel temperature over a range of energies up to 44 meV and at a few temperatures up to 650 K. They found no evidence of paramagnetic-diffuse scattering, thus confirming earlier work[38] which showed the absence of disordered local spins in the paramagnetic state of chromium. On the other hand, they observed commensurate-diffuse scattering, which begins in the transverse SDW phase, peaks at a temperature a little above the Néel transition, and persists throughout the paramagnetic phase. They put their measurements on an absolute basis by normalizing the inelastic scattering to the integrated intensity of selected phonons. They were thus able to evaluate the effective moment μ_{eff}, which is equivalent to the root-mean-square moment, i.e., $\mu_{\text{eff}}^2 = \langle M^2 \rangle$ in our notation, at three temperatures in the paramagnetic phase.

Their results are plotted in Fig. 3, where we show the temperature dependence of the neutron scattering intensity in comparison with that of the magnetovolume. Ziebeck, Booth, Brown, Capellman, and Bland[37] have reported commensurate-diffuse scattering up to a temperature of 687 K but we have not included their results in Fig. 3, since the normalization procedure they used gave values of $\langle M^2 \rangle$ up to 100 times smaller than those of Grier, Shirane, and Werner[7] who state that the discrepancy may result from an improper treatment in the earlier work[37] of the effects of the shape and orientation of the resolution function in their polarized beam studies.

Well below the Néel transition, the magnetovolume roughly follows the temperature dependence of $\langle M^2 \rangle$, but begins to deviate as the Néel temperature T_N is approached. Thus when the elastic scattering has virtually disappeared just above T_N (see Fig. 10 of Ref. 7) the magnetovolume is still about 25% of the ground-state value. Some of this discrepancy between the temperature changes of ω_M and of the mean-square-*ordered* moment occurs in the first order change at T_N, where $\Delta\omega_M/\omega_M(0) \simeq 2\%$, while $\Delta\langle M^2 \rangle / \langle M^2(0) \rangle \simeq 6\%$. Most of the deviation between the curves occurs, however, as the temperature increases from about 30 K below T_N, peaking at T_N and then decreasing more slowly to zero at about 250 K above T_N.

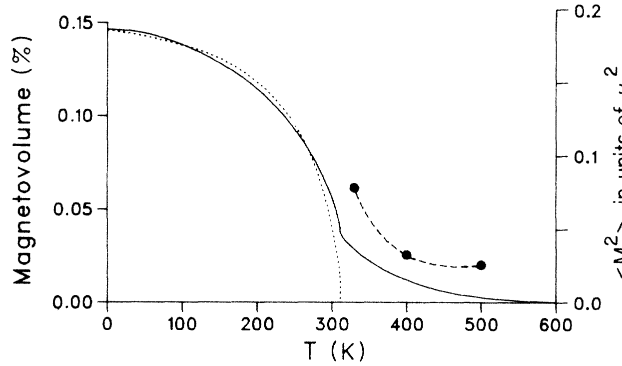

FIG. 3. Temperature dependence of the mean-square magnetic moment $\langle M^2 \rangle$ compared with the magnetovolume ω_M of chromium (and dashed line which is sketched as a guide to the eye) show $\langle M^2 \rangle$ in the paramagnetic phase (Grier *et al.*); the dotted line shows the temperature dependence of $\langle M^2 \rangle$ in the antiferromagnetic phase (data of Werner *et al.* smoothed in accordance with the remarks in Sec. III); the solid line shows the magnetovolume $\omega_M(T)$, which is normalized so that the curves coincide at zero temperature. The right-hand ordinate axis is scaled according to the ratio $\omega_M(0)/\Delta\langle M^2 \rangle = 0.90\% \mu_B^{-2}$.

The cause of this deviation becomes clearer when we consider the evolution with temperature of the inelastic neutron scattering. In the transverse SDW phase at a temperature as low as 200 K Grier, Shirane, and Werner[7] observed commensurate-diffuse scattering with a characteristic energy of 4 meV superimposed on a quasielastic background. The latter increases very rapidly with decreasing energy (hence the description as "quasielastic") and also with increasing temperature as T_N is approached. This quasielastic component appears to be diverging at T_N, and in fact increases exponentially over the range of temperatures from 200 to 300 K. In the neighborhood of T_N, the modes of excitation responsible for the inelastic scattering overwhelm the ordered structure of antiferromagnetic chromium, all traces of which have disappeared by about 15 K above T_N, while the commensurate-diffuse scattering persists as we have seen up to at least 700 K.

Thus we can understand the temperature dependence of the magnetovolume in Fig. 3 if we suppose that it is determined well below T_N by the mean-square-*ordered* moment of the incommensurate SDW and in the neighborhood of T_N and above T_N by the mean-square *fluctuating* commensurate moment. The magnetovolume ω_M above T_N is somewhat less than would be expected from the values of $\langle M^2 \rangle$ determined by Grier, Shirane, and Werner[7] and there is little magnetovolume left at 500 K, while the value of $\langle M^2 \rangle$ is still about 15% of the ground-state value.

A possible cause of this discrepancy between the high-temperature thermal expansion and the inelastic neutron scattering data shown in Fig. 3 may be Moriya-type spin fluctuations. In the self-consistent renormalization theory of spin fluctuations[25] a fluctuating magnetic moment appears, whose mean square increases linearly with temperature, giving, according to Eqs. (1) and (5), a constant positive contribution α_{SF} to the high-temperature thermal expansivity.[26] One might expect that, if such a term appears in pure Cr, it would be essentially identical in magnitude in $Cr_{95}V_5$ (and in the dilute antiferromagnetic CrV alloys) at temperatures well above the Néel transition of Cr. Thus the difference method we have used to obtain the magnetic contribution to the thermal expansion fails when, as in the case of spin fluctuations, the two contributions are identical, i.e., $\alpha_{A(SF)} \equiv \alpha_{P(SF)}$ (or for pure Cr, $\alpha_{(SF)} \equiv \alpha_{P(SF)}$) on the right-hand side of Eq. (6).

However, discounting the problems Ziebeck, Booth, Brown, Capellman, and Bland[37] encountered in calibrating their measurements to obtain absolute values of $\langle M^2 \rangle$, we note from Fig. 1 of Ref. 37 that the commensurate-diffuse scattering is considerably reduced at temperature 687 K below its value at temperature 473 K. Thus in Fig. 3 we should expect $\langle M^2 \rangle$ to continue to decrease beyond 500 K. This means that paramagnetic spin fluctuations are unlikely to be responsible for low-energy commensurate-diffuse scattering in chromium.

One might think that the Grüneisen parameter γ_{HT} being of order unity at high temperatures (see Table II in Ref. 16), in contrast with the very large values associated with magnetic ordering as listed in Table I, means that the contribution of spin fluctuations to the thermophysical properties of chromium is negligible. The small specific-heat anomaly associated with magnetic ordering (see Fig. 2) shows however that the energy of the SDW ground state is only a little below that of the paramagnetic state, whereas spin fluctuations may well be associated with the high-energy excitations, which persist up to at least 500 K in the paramagnetic state without apparently diminishing in intensity, as shown in Fig. 4. The large Grüneisen parameters mean that the magnetoelastic coupling associated with the relatively low energy excitations responsible for destruction of magnetic order with increasing temperature is very strong. There is no apparent reason however why this should be true also for the high-energy excitation observed at high temperatures in the paramagnetic state.

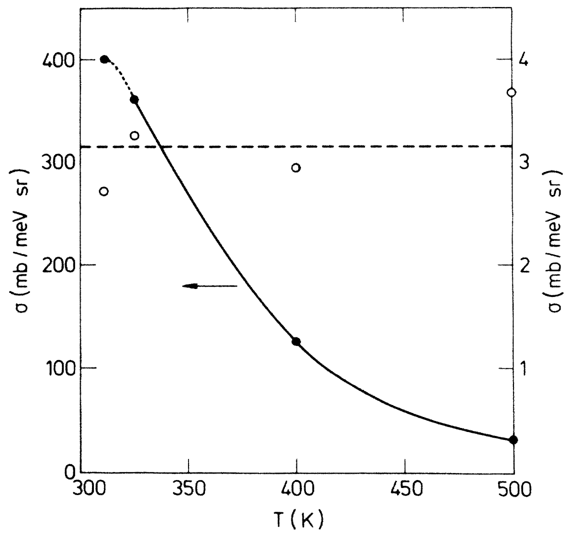

FIG. 4. Temperature dependence of the neutron scattering cross section σ corresponding to the magnetic fluctuations per unit energy E for chromium measured at energy $E = 2$ meV (● and left-hand scale) and energy $E = 44$ meV (○ and right-hand scale) as estimated from the data of Grier *et al.*

VII. MAGNETOELASTIC COUPLING CONSTANT

In order to obtain an experimental value of the magnetoelastic coupling constant C defined in Eq. (1), we need to relate the change in magnetovolume ω_M to the change in mean-square moment $\langle M^2 \rangle$, keeping in mind that the bulk modulus is assumed in this definition to be equal to the zero-temperature value B_0. When comparing experimental data it is more convenient to incorporate the bulk modulus into the definition and consider the quantity C/B, where B is some average value of the bulk modulus for the temperature interval over which the changes in ω_M and $\langle M^2 \rangle$ are measured.

We must keep in mind also that the magnetovolume $\omega_M(T)$ in Cr is defined in Eq. (4) relative to that in the paramagnetic alloy $Cr_{95}V_5$. Kaiser and Haines[22] argued that $\omega_M(T)$ is zero for $T \gtrsim 600$ K, this being the temperature at which the expansivities of Cr, $Cr_{99.5}V_{0.5}$, and $Cr_{95}V_5$ are essentially identical. They thus would associate the mean-square-ordered moment, $\frac{1}{2}M_0^2 = 0.185\mu_B^2$ ($M_0 = 0.62\mu_B$ being the amplitude of the SDW in Cr at low temperatures[39]) with the ground-state magnetovolume, $\omega_0 = 0.143\%$, obtained by integrating the thermal expansivity difference $\alpha_M(T)$ from $T_h = 700$ K to zero temperature, as illustrated in Fig. 3. This gives a value, $C/B = 0.8\%\ \mu_B^{-2}$.

If the commensurate-diffuse scattering corresponding to a mean-square moment of $0.026\mu_B^2$ at 500 K as observed by Grier, Shirane, and Werner[7] is absent in paramagnetic $Cr_{95}V_5$, then the *change* in $\langle M^2(T) \rangle = (0.185 - 0.026)\mu_B^2 = 0.159\mu_B^2$ [with $\langle M^2(500) \rangle = 0.026\mu_B^2$ according to Grier, Shirane, and Werner[7]] should be associated with the magnetovolume difference, $\omega_0 = 0.141\%$ (the magnetovolume between 500 and 700 K being $\Delta\omega_M \simeq 0.002\%$). This gives a value $C/B = 0.9\%\ \mu_B^{-2}$, which we shall adopt.

We note that, with the bulk modulus B having its low-temperature value, $B_0 = 195$ GPa,[16] one obtains $C = 17$ kbar$\,\mu_B^{-2}$, as in Table I of Kaiser and Haines.[22] One might argue, however, that a somewhat smaller high-temperature value of B should be used to evaluate C from the quantity $\omega / \langle M^2 \rangle$ determined experimentally.

We may compare this experimental value of C/B with the value obtained from the theory of Holden, Heine, and Samson[21] by substituting in Eq. (3), $I=56$ mRy and $B_0V_0=1070$ mRy, corresponding to $B_0=195$ GPa, to obtain $C/B=2.2\%\ \mu_B^{-2}$. We note that different theoretical estimates of I for chromium range from 51 to 62 mRy (Table IV of Ref. 40) so that the value chosen by Holden, Heine, and Samson[21] is unlikely to be wrong by more than 10%. We note also that they use a value, $B_0V_0=880$ mRy, apparently based on the minimum value of the bulk modulus $B=162$ GPa at the Néel transition of Palmer and Lee.[41] Since the appropriate value of B is somewhere between these two extremes (see Fig. 4 of Ref. 16), a better estimate might be about 10% higher, $C/B\simeq 2.4\%\ \mu_B^{-2}$.

Other theoretical estimates of the ground-state magnetovolume quoted by Kaiser and Haines[22] and hence, with the use of the calculated or experimental value of $\langle M_0^2\rangle$, estimates of C/B, give values ranging from $C/B=0.8-6.6\%\ \mu_B^{-2}$. Kübler's[42] value, corresponding to his estimate, $\omega_0=0.15\%$ (quoted by Kaiser and Haines[22]), appears to be in excellent agreement with the experimental values of C/B. Skriver[40] has pointed out however that all calculations in the local-spin-density approximation (LSDA) are very sensitive to the arbitrary choice of exchange-correlation potential. We shall therefore continue to base our discussion on the theory of Holden, Heine, and Samson,[21] which is more physically transparent than the LSDA calculations.

The simplest explanation for the discrepancy between the experimental and theoretical values of $C/B=\omega_0/\langle M^2\rangle$, 0.9 and 2.4% μ_B^{-2}, respectively, is that instead of the canonical value $\beta_1=d\ln N/d\omega=\frac{5}{3}$ for a d-band model without hybridization employed by Holden, Heine, and Samson,[21] the correct value for paramagnetic Cr is considerably smaller, say $\frac{1}{2}$. This gives, with $-\beta_1\beta_2=d\ln I/d\omega=0$, a value, $C/B\simeq 2.4\times\frac{3}{10}\simeq 0.75\%$ μ_B^{-2}, in rough agreement with experiment. Measurements of the strain dependence of the Fermi surfaces of the homologous metals Mo (Ref. 43) and W (Ref. 44) yield such lower values,[45] $d\ln N/d\omega=0.7$ and 0.2, respectively. After making a correction for the volume dependence of the electron-phonon interaction,[46] Griessen[45] obtained excellent agreement with the experimental values of the electronic Grüneisen parameter obtained from the low-temperature thermal expansion,[47,48] $\gamma_e=1.1$ and 0.3 for Mo and W, respectively. Kulikov and Kulatov[49] and Kübler[42] calculated the band structure of Cr for different lattice parameters, thereby providing rather different theoretical estimates, $\beta_1=0.3$ and 2, respectively. A value, $\beta_1=1.6$, is obtained if we use the experimental value,[16] $\gamma_e=2.0$, for $Cr_{95}V_5$ to provide an estimate for the Grüneisen parameter of paramagnetic Cr and make a correction for the volume dependence of the electron-phonon interaction.

We next consider negative volume dependence of the exchange interaction parameter I, giving $\beta_1\beta_2>0$ in Eq. (2), which with $\beta_1>0$, reduces the theoretical value of the magnetoelastic coupling constant C in Eq. (6). It can be seen from these equations that C/B would be reduced from $2.4\mu_B^{-2}$ to $0.9\mu_B^{-2}$ in agreement with experiment if, with $\beta_1=\frac{5}{3}$, we make $\beta_1\beta_2=-d\ln I/d\omega=1.0$.

Such a large value of $-d\ln I/d\omega$ is not expected from local spin-density functional calculations.[50] Earlier, however, Kanamori[51] had calculated an effective exchange interaction with a relatively large volume dependence, the bare intra-atomic Coulomb interaction I_0 being reduced by an increase in screening as volume increases to give an effective interaction

$$I=\frac{I_0}{1+(gI_0/W)}\ , \tag{13}$$

where g is a constant of order unity. For I_0 of the same order of magnitude as the bandwidth W, i.e., $I\simeq I_0/2$, with $d\ln W/d\omega\simeq -d\ln N/d\omega=-\frac{5}{3}$ and I_0 and g independent of volume, we obtain $d\ln I/d\omega=-\frac{5}{6}$. This is just about the right magnitude to reconcile the calculation of Holden, Heine, and Samson[21] with experiment. Shimizu,[52] using Kanamori's I, has deduced even greater reductions in magnetovolume owing to the dependence of I. We note[22] that a volume dependence of I with $d\ln I/d\omega\simeq -1$ appears to be implicit in the successful calculations of Kübler.[42]

We mention three further pieces of experimental evidence for a volume-dependent I. Fawcett and Pluzhnikov[53] found that the susceptibility χ of Pd*Rh* alloys was less volume dependent than expected from the Stoner relation

$$\chi=\frac{\chi_0}{1-N(0)I}\ , \tag{14}$$

where χ_0 is the bare susceptibility. They attributed this effect to a strong volume dependence of I, with $d\ln I/d\omega\simeq -2.5$. Mathon,[54] analyzing the observed pressure dependence of magnetization in Ni within the Stoner model, deduced $d\ln I/d\omega\simeq -1$ and $I/I_0\sim 0.4$. Finally, Kortekaas and Franse[55] found values of the magnetoelastic coupling constant C from forced magnetostriction in nearly or weakly ferromagnetic Ni-based alloys that were lower than those expected for $\beta_1=\frac{5}{3}$ and $\beta_2=0$. For Ni_3Al alloys they deduced a strong volume dependence for I, with $d\ln I/d\omega\simeq -0.8\pm 0.2$, but for NiPt alloys, only a weak dependence $d\ln I/d\omega=-0.2\pm 0.1$ was obtained. It seems, therefore, that our experimental value of ground-state magnetovolume can be understood within the model of Holden, Heine, and Samson[21] with a volume-dependent effective exchange interaction.

VIII. CONCLUSIONS

We have shown that thermal expansion measurements over a wide temperature range, combined with specific-heat and neutron scattering data, shed a good deal of light on magnetic effects in chromium. Our main conclusions can be summarized as follows:

The Grüneisen parameters associated with the decay of magnetic order in chromium and dilute Cr*V* alloys are large and negative; however, the Grüneisen parameter in the paramagnetic state at high temperatures shows more normal behavior, being positive and much smaller.

The discontinuity in volume at the first order Néel transition at T_N in pure chromium is much smaller than the corresponding discontinuity in the ordered moment as measured by neutron scattering. The volume discontinuity and latent heat at T_N in Cr are however consistent with the Clausius-Clapeyron relation. In Cr + 0.5 at. % V the Néel transition appears to be continuous.

The decay of magnetovolume $\omega_M(T)$ above T_N is rather similar to the decay of the mean-square moment $\langle M^2(T) \rangle$ measured by inelastic neutron scattering, except that above temperature about $T \simeq 600$ K, there is no difference in the thermal expansions of Cr and the paramagnetic alloy $Cr_{95}V_5$, whereas at 500 K the mean-square moment, $\langle M^2 \rangle \sim 0.026 \mu_B^2$, is still an appreciable fraction of the ground-state value $\frac{1}{2} M_0^2 = 0.185 \mu_B^2$. Further high-temperature neutron measurements, particularly on $Cr_{95}V_5$ which has no long-range order, would be of great interest to clarify the relation between neutron scattering and thermal expansion.

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