Magnetoelastic Properties of Single-S, Single-Q Chromium

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When new data for the elastic stiffness tensor of single-polarization, single-wave-vector chromium are combined with volume thermal expansion, the magnetic free energy is found to be a function of reduced temperature, T/T_N; the dependence of the Néel temperature T_N on longitudinal strain is much stronger than on shear strain, and is linear in strain and nearly isotropic. Grüneisen parameters defined at and below T_N being roughly constant validates this single-parameter model.

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Definitive experimental data[1] for the components c_{ij} of the elastic stiffness tensor of antiferromagnetic chromium in the single-polarization (single **S**), single-wave-vector (single **Q**) state, briefly reported here, have thrown new light on an old problem. Bolef and de Klerk,[2] in their pioneering experimental study of polycrystalline Cr, recognized the close connection between the temperature dependence of the magnetic anomalies in c_{ij} and that of the thermal expansion in the transverse spin-density-wave (TSDW) phase and at the two magnetic phase transitions.

Walker[3] developed a phenomenological theory of the SDW in Cr with a Ginzburg-Landau Hamiltonian set up in accordance with the symmetry of the cubic paramagnetic phase, and minimized to give terms corresponding to the TSDW phase. His predictions about the nature of the magnetic anomalies in the various elastic moduli at the Néel temperature T_N have remained largely untested, despite refinements of the experiments on single-crystal samples,[4-7] since the work of Bolef and de Klerk.[2]

We present here a preliminary report on the first experimental study[1] of the elastic moduli of single-**S**, single-**Q** Cr. We note that, while this is not the ground state of the TSDW phase of Cr, it has the same excitation spectrum as single-**Q** Cr, as determined by inelastic neutron scattering,[8] and should therefore be amenable to thermodynamic analysis as though it were the ground state.

The single-crystal sample was cut from an arc-melted boule, which had been annealed for 72 h at 1550 °C. Field cooling in a magnetic field of 12 T, along the [001] cube axis, gave a 97% single-**Q** state, as determined by neutron diffraction. The single-**S** state of the TSDW phase was achieved by means of a transverse polarizing field, **H** = 5 T, along the [010] axis. Our results provide strong supporting evidence for conclusions that can already be seen to follow from the early results,[2] namely, that the longitudinal-strain dependence of the magnetic free energy ΔF is much greater than the shear-strain dependence, that the strain dependence of ΔF is mainly a volume dependence, and that ΔF is an approximately linear function of volume strain for small strains. The data at T_N also confirm qualitatively Walker's[3] predictions about the relative magnitudes of the anomalies in the various components of the stiffness tensor at the Néel transition.[1]

We shall write the magnetic free energy $\Delta F(t)$ as the difference between the Helmholtz free energies $F^L(t)$ in

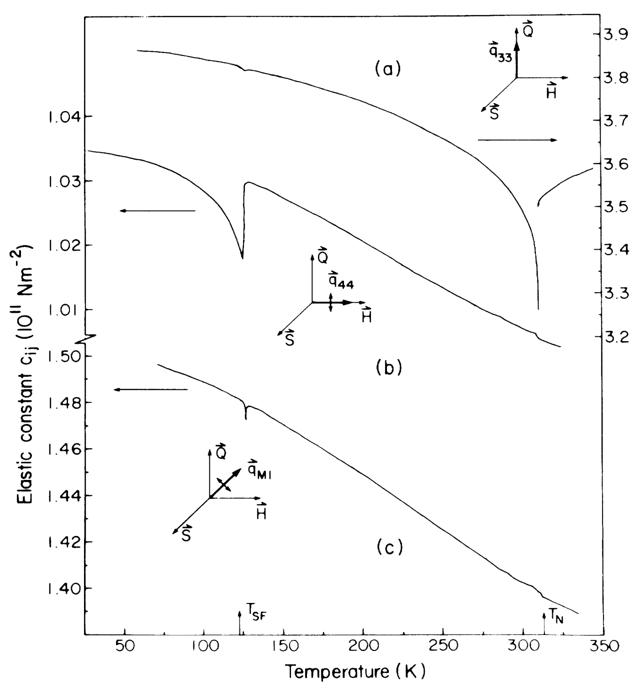

FIG. 1. Temperature dependence of typical elastic moduli in orthorhombic single-**S**, single-**Q** chromium from just above the Néel temperature, $T_N = 312$ K, to temperatures well below the spin-flip temperature, $T_{sf} \simeq 125$ K. Curve a, c_{33} typical of the longitudinal moduli c_{ii} $(i = 1,2,3)$; curve b, c_{44} typical of the shear moduli $c_{\alpha\alpha}$ $(\alpha = 4,5,6)$; curve c, c_{M1} typical of the quasishear moduli c_{Mi} $(i = 1,2,3)$. Insets: The directions of the polarizing field **H**, the ultrasonic wave vector $\mathbf{q}_{ij}$, and, in the case of transverse waves, the displacement direction. **Q** and **S**, respectively, show the wave-vector and polarization directions of the SDW.

the low-temperature (L) ordered phase and $F^H(t)$ in the high-temperature (H) disordered phase, extrapolated into the low-temperature region:

$$\Delta F(t) = F^H(t) - F^L(t) = \phi f(t(\epsilon_i)), \quad (1)$$

with $t = T/T_N(\epsilon_i)$. Here, following Testardi,[9] ϕ is a positive constant, $f(t)$ is an undetermined function of the reduced temperature t, ϵ_i are components of the strain tensor, T is the temperature, and $T_N(\epsilon_i)$ is the strain-dependent Néel temperature.

The disordered phase of Cr exhibits magnetic anomalies well above T_N in both the thermal expansion[10] and the elastic moduli,[5,6] so that in practice the reference system used instead of the high-temperature disordered phase of Cr is the alloy $Cr_{95}V_5$. This alloy is paramagnetic, but otherwise might be expected to be close to Cr in its thermophysical properties, so that effectively it may be regarded as "paramagnetic chromium." Accordingly, we denote by Δ the difference between $Cr_{95}V_5$ and Cr.

The magnetic contributions, denoted ΔC_v, etc., to the specific heat C_v, the fractional volume change ω, the thermal expansivity β, the elastic moduli c_{ij}, and the bulk modulus B, in terms of the first and second derivatives, $f'(t)$ and $f''(t)$, respectively, are obtained from the magnetic free energy $\Delta F(t)$ defined in Eq. (1):

$$\Delta C_v(t) = -(t/T_N)\partial^2\Delta F/\partial t^2 = -\phi t f''(t)/T_N, \quad (2a)$$

$$\Delta\omega(t) = -[B(t)]^{-1}\partial\Delta F/\partial\omega = [\phi/B(t)](\partial \ln T_N/\partial\omega) t f'(t), \quad (2b)$$

$$\Delta\beta(t) = T_N^{-1}\partial\Delta\omega/\partial t = [\phi/B(t)]T_N^{-1}(\partial\ln T_N/\partial\omega)[f'(t)+tf''(t)], \quad (2c)$$

$$\Delta c_{ij}(t) = \partial^2\Delta F/\partial\epsilon_i\,\partial\epsilon_j = \phi\{(\partial\ln T_N/\partial\epsilon_i)(\partial\ln T_N/\partial\epsilon_j)t[2f'(t)+tf''(t)] - T_N^{-1}(\partial^2 T_N/\partial\epsilon_i\,\partial\epsilon_j)tf'(t)\}, \quad (2d)$$

$$\Delta B(t) = \tfrac{1}{3}[\Delta c_{11}(t) + 2\Delta c_{12}(t)]. \quad (2e)$$

The magnetovolume $\Delta\omega$ in Eq. (2b) is obtained from ΔF in the good approximation[5] that B is constant over the range of variation of $\Delta\omega$. In Eq. (2c) the term involving the derivative of $B(t)$ is neglected, since in Cr the fractional change in $B(t)$ with temperature is known from experiment[1] to be small relative to that in $\Delta B(t)$.

We now make the following assumptions: (1) The shear-strain dependence of $T_N(\epsilon_i)$ is much weaker than the longitudinal-strain dependence,

$$\frac{\partial\ln T_N}{\partial\epsilon_\alpha} \ll \frac{\partial\ln T_N}{\partial\epsilon_i} \quad (i=1,2,3;\ \alpha=4,5,6); \quad (3)$$

(2) the longitudinal-strain dependence of $T_N(\epsilon_i)$ is almost isotropic and mainly a volume dependence,

$$\partial\ln T_N/\partial\epsilon_i \simeq \partial\ln T_N/\partial\omega; \quad (4)$$

(3) $T_N(\epsilon_i)$ is approximately linear for small strains,

$$T_N^{-1}\partial^2 T_N/\partial\epsilon_i\,\partial\epsilon_j \ll \partial\ln T_N/\partial\epsilon_i. \quad (5)$$

The near isotropy expressed in Eq. (4) follows from the experimental results[11,12] that the discontinuity in ϵ_i at the weak first-order transition at T_N is isotropic to an accuracy of about 5%, and that the anisotropy of $\epsilon_i(t)$ below T_N is nowhere greater than about 1.5% of $\Delta\omega(t)$. In Walker's theory,[3] the shear-stress dependence of T_N is identically zero [cf. (3)], while linearity corresponds to neglect of terms quadratic in stress, and the near isotropy of stress dependence of T_N [cf. (4)] means that the spin-orbit interaction is much weaker than the exchange interaction.

With these assumptions, Eqs. (2) give

$$\Delta c_{\alpha\alpha} \ll \Delta c_{ij}, \quad (6a)$$

$$\Delta c' = \Delta\tfrac{1}{2}(c_{11}-c_{12}) \ll \Delta c_{ij}, \quad (6b)$$

$$\Delta B(t) = \phi(\partial\ln T_N/\partial\omega)^2 t[2f'(t)+tf''(t)], \quad (6c)$$

where Eq. (6c) follows from Eq. (2e) in the light of the inequality (5) and the experimental fact[5] that $\partial\ln T_N/\partial\omega \gg 1$.

A selection of the experimental data[1] for the elastic moduli obtained by continuous tracking of the ultrasonic velocity is shown in Fig. 1. It is evident from inspection that the magnetic anomaly, both above and at T_N, and in the TSDW phase between T_N and T_{sf}, is much larger for c_{33} than for either c_{44} or c_{M1}. The same is true[1] when the other longitudinal moduli, c_{ii} ($i=1,2,3$), are compared with the shear moduli, $c_{\alpha\alpha}$ ($\alpha=4,5,6$), and the quasishear moduli c_{Mi} ($i=1,2,3$). The magnetic anomalies at the spin-flip transition will be discussed elsewhere.[13]

The quasishear modulus c_{M1} in an orthorhombic system, expressed in terms of the components c_{ij} of the elastic stiffness tensor, is

$$c_{M1} = \tfrac{1}{4}(c_{22}+c_{33}+2c_{44}) - \tfrac{1}{2}[(c_{23}+c_{44})^2 + \tfrac{1}{4}(c_{22}-c_{33})^2]^{1/2}. \quad (7)$$

Single-**S**, single-**Q** Cr is orthorhombic in the TSDW phase, but the deviations of c_{ij} from a cubic tensor are small,[1] i.e.,

$$c_{ii} \simeq c_{11};\quad c_{ij} \simeq c_{12};\quad c_{\alpha\alpha} \simeq c_{44} \quad (i=1,2,3;\ \alpha=4,5,6). \quad (8)$$

Thus to a good approximation Eq. (7) becomes

$$c_{M1} \simeq \tfrac{1}{2}(c_{11}-c_{12}). \tag{9}$$

We can now see how the experimental data shown in Fig. 1 corroborate the assumptions about the strain dependence of $T_N(\epsilon_i)$ expressed in Eqs. (3), (4), and (5), which lead to Eqs. (6). In brief, curve *a* in Fig. 1 exemplifies the application of Eq. (6c), while curves *b* and *c* exemplify the application of Eqs. (6a) and (6b), respectively, in the light of Eq. (9).

We note in Fig. 1 that at T_N the magnetic anomaly $\Delta c_{33}(T_N)$ is considerably larger than those in c_{44} and c_{M1}, the same being true[1] for the other components:

$$\Delta c_{ii}(T_N) \gg \Delta c_{aa}(T_N) \simeq \Delta c_{Mi}(T_N). \tag{10}$$

These results agree qualitatively with the predictions of Walker's[3] theory.

We shall publish elsewhere[14] an account of the several different Grüneisen parameters that can be defined to describe[15] various aspects of the behavior of antiferromagnetic Cr. We note here that comparison of Eq. (2c) with Eq. (6c) enables us to define a temperature-dependent Grüneisen parameter,

$$\gamma(t) = -[T_N B(t)]^{-1}\Delta B(t)/\Delta\beta(t) = -\frac{\partial \ln T_N}{\partial \omega} t \frac{[2f'(t)+tf''(t)]}{[f'(t)+tf''(t)]}. \tag{11}$$

The data of Alberts and Lourens[16] for the temperature dependence of the bulk modulus of polycrystalline $Cr_{95}V_5$ was used for comparison with Cr, obtained from our data by means of Eq. (2e), to determine $\Delta B(t)$. It is surprising to find that, throughout the TSDW phase, $\Delta B(t)$ and $\Delta\beta(t)$ vary linearly with slope 2.4×10^{15} N K m^{-2}, as shown in Fig. 2. One might, however, expect the inequality $|f'(t)| \ll |f''(t)|$ to hold at temperatures close to T_N since $f'(t)$ approaches zero as temperature approaches the almost continuous Néel transition, while $f''(t)$ remains finite and positive. For example, the function $f(t)=(1-t^2)^2$, used by Testardi[9] to illustrate his thermodynamic relations, gives $f'(t)/f''(t) \simeq -\delta t$ for $t=(1-\delta t)$, so that Eq. (11) gives

$$\gamma(t \lesssim 1) \equiv \gamma_{T_N}^- \simeq -\partial \ln T_N/\partial\omega. \tag{12}$$

The bulk modulus of the $Cr_{95}V_5$ alloy varies less than 1% below the Néel temperature,[16] so that if we use its average value, $B_A^- = 2.07\times10^{11}$ N m^{-2}, in place of $B(t)$ with $T_N = 312$ K in Eq. (11), we obtain a Grüneisen parameter $\gamma_{T_N}^- = -37$.

This value is roughly equal to the Grüneisen parameter obtained[15] directly from the pressure dependence of the Néel temperature,[5]

$$\gamma_{T_N} = -\frac{\partial \ln T_N}{\partial \omega} = \frac{B(T_N)}{T_N}\frac{dT_N}{dp} = -28. \tag{13}$$

We find also that both $\gamma_{T_N}^-$ and γ_{T_N} are of the same order of magnitude as the zero-temperature Grüneisen parameter,[14]

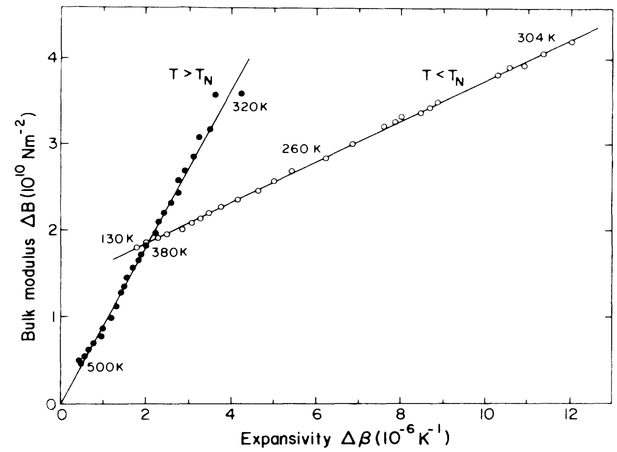

FIG. 2. Comparison of the magnetic anomalies of the bulk modulus $\Delta B(t)$ and the volume thermal expansivity $\Delta\beta(t)$ in chromium. Open circles, below the Néel transition in the temperature range 130 to 304 K; filled circles, above the Néel transition in the temperature range 320 to 500 K. Both $\Delta B(t)$ and $\Delta\beta(t)$ are obtained by comparison of chromium with the paramagnetic alloy $Cr_{95}V_5$, whose thermal expansivity was measured by White, Roberts, and Fawcett (Ref. 10), and bulk modulus by Alberts and Lourens (Ref. 16). The data of Katahara *et al.* (Ref. 5) for the elastic constants of Cr up to 700 K were used for $T > T_N$.

$$\gamma_0 = \Delta B_0/B_0\Delta\omega_0 = -60. \tag{14}$$

The ground-state magnetovolume, $\Delta\omega_0 = -1.43\times10^{-3}$, is obtained[15] by integration of the difference between the thermal expansivities of $Cr_{95}V_5$ and Cr and extrapolation to $t=0$. To determine the difference between the bulk moduli, $\Delta B_0 = 1.75\times10^{10}$ N m^{-2}, we follow the procedure of Alberts and Lourens[16,17] by adjusting the bulk modulus $B_A(T)$ for $Cr_{95}V_5$ (subscript A denoting alloy) so as to make the curve for its temperature dependence asymptotic to $B(T)$ for Cr, and then extrapolate to $t=0$. This nonzero value of ΔB at zero temperature corresponds to the strain dependence of the prefactor ϕ in Eq. (1), which is neglected in the present work, but is included in Testardi's analysis.[9]

In the paramagnetic phase also, $\Delta B(T)$ and $\Delta\beta(T)$ give a linear plot, with a slope 9.1×10^{15} N K m^{-2}. The data[16] for the bulk modulus $B_A(T)$ of $Cr_{95}V_5$ are adjusted so as to make the line for $T > T_N$ in Fig. 2 go through the origin. $B_A(T)$ decreases by about 3% in this temperature interval, and the average value, $B_A^+ = 2.03\times10^{11}$ N m^{-2}, gives a Grüneisen parameter $\gamma_{T_N}^+ = -144$. The much larger value of the Grüneisen parameter above T_N indicates that the short-range magnetic order and magnetic fluctuations in the disordered phase of Cr[8] are even more volume dependent than is the SDW in the antiferromagnetic phase.

The fact that the magnetic free energy may be expressed by a single, strongly volume-dependent parameter T_N makes Cr a model system for application of our method for measurement of a large Grüneisen parameter by comparison of the magnetic contributions to the bulk modulus and the thermal expansivity. We are currently using this method, for example, to see if low-frequency modes involving volume strain are important in high-temperature superconductors. Finally, the very large Grüneisen parameter found in the paramagnetic phase focuses our attention on this interesting highly correlated magnetic state,[8] and further studies of inelastic scattering in pure Cr and dilute Cr:V alloys are in progress.

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