range 7 to 25 L [Figs. 2(b) and 2(c)] the following effects are observed: (i) The oxygen-derived levels gradually increase in amplitude and broaden, (ii) the work function decreases, and (iii) Ni d-band emission within 3.3 eV of E_F decreases. At exposures of 23 L (curve 5) and 59 L (curve 6), emission from metallic Ni has diminished to $\lesssim \frac{1}{3}$ its initial value, and emission from oxygen-derived levels is seen in the range from about 2.5 to 11 eV below E_F, with structure observed at about 5, 7, and 10 eV below E_F. We associate this structure with the filled $2p$ bands of our surface oxide. A new energy level at 2 eV below E_F is seen for exposures $\gtrsim 23$ L. This level, which is more clearly seen at $h\nu = 40.8$ eV (curve 6b), is attributed to the d electrons of oxidized Ni [probably $\mathrm{Ni}^{2+}(d^8)$]. The observed increase of this $-$2-eV level with increasing $h\nu$ by about a factor of 2 relative to the lower-lying $2p$ bands is consistent with emission from d states relative to p states, since the latter tend to saturate their oscillator strengths at lower photon energies.[4]

In summary, our measurements for CO and O adsorbed on Ni show that photoemission spectroscopy has considerable promise as a general technique for measuring energy levels associated with adsorption and other surface reactions. Fruitful extensions of these measurements might include the use of well-characterized single-crystal substrates, low-temperature measurements which should permit both physisorption measurements as well as chemisorption measurements of species which do not adsorb in appreciable quantities at room temperature, and, perhaps of most interest, studies of catalytic surface reactions in which surface energy levels can be measured via photoemission spectroscopy while catalytic activities are measured via mass spectroscopy or other suitable methods.

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[6] The amplitude of this -10.7-eV level is attenuated due to the low transmission of the electron analyzer at this low kinetic energy (~5 eV), and the background is mainly due to secondary emission from the analyzer. The relative amplitudes of the CO levels are shown in Fig. 1(b) for $h\nu = 40.8$ eV. All energy distribution curves are uncorrected for the analyzer transmission factor, which increases linearly with increasing kinetic energy for energies $\gtrsim 7$ eV.

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First-Order Transition in Chromium at the Néel Temperature*

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A latent heat, hysteresis, and superheating and supercooling have been observed in a Cr single crystal by means of an extension of the ac calorimetric method.

Although neutron-diffraction studies revealed a first-order transition in Cr at $T_N = 311$ K,[1] other manifestations of the first-order nature are rare. The transition is usually smeared over a few tenths of a degree and looks like a second-order phase change.[2] Recently, however, Sze and Meaden[3] have observed a large (50%) step in specific heat and a cooling plateau in a polycrystalline sample, from which they estimate a latent heat of 0.47 cal/mole. We report here the results of a more direct measurement on a well-annealed 7-mg single crystal, using an extension of the ac calorimetric method to determine the latent heat and specific heat simultaneously.

Expansivity data for Cr, interpreted as a manifestation of a first-order transition, enable us to estimate the latent heat from the Clausius-Clapeyron equation, with the result[4]

$$L_e = 0.23 \pm 0.05 \text{ cal/mole}. \tag{1}$$

Another estimate exploits the neutron-diffraction data on the square of the spin-density-wave amplitude.[1] Using the Landau expansion[5] of the free energy in terms of the order parameter η and the constants a, B (<0), and G,

$$\varphi = \varphi_0 + a(T - T_0)\eta^2 + B\eta^4 + G\eta^6,$$

we may determine the step change in the specific heat ΔC_p and the latent heat. Stability and continuity of φ lead to the results[5]

$$\begin{aligned} &\Delta C_p = a^2 T_{\mathrm{N}}/|B|, \quad L = a|B|T_{\mathrm{N}}/2G, \\ &T_{\mathrm{N}2} = T_{\mathrm{N}} + B^2/2aG, \end{aligned} \tag{2a}$$

for a first-order transition at $T_{\mathrm{N}} > T_0$. The temperature $T_{\mathrm{N}2}$ corresponds to the point at which the $\eta^2(T)$ curve extrapolates to zero. Equations (2a) may be combined to give

$$L_n = \Delta C_p(T_{\mathrm{N}2} - T_{\mathrm{N}}). \tag{2b}$$

Estimating $T_{\mathrm{N}2} - T_{\mathrm{N}} = 2.5 \pm 0.5$ K from the neutron data[1] and $\Delta C_p = 0.1 \pm 0.01$ cal/mole K from an extrapolation of the behavior outside the critical region,[2] we find

$$L_n = 0.25 \pm 0.08 \text{ cal/mole}, \tag{3}$$

in agreement with the expansivity estimate (1).

The sample used in this study was a thin plate (2×3×0.15 mm), weakly coupled to a heat sink by an exchange gas. Heat pulses were provided by a light source chopped at a frequency f. The dynamic behavior of the system involves two characteristic time constants: τ_1, which characterizes the thermal coupling between the specimen and its surroundings, and τ_2, the time for the sample to reach internal thermal equilibrium.[6] When

$$f\tau_2 \gg 1, \tag{4}$$

the sample temperature $T(t)$ satisfies the equation

$$C\dot{T} + kT = \tfrac{1}{2}P_0[1 + s(t)], \tag{5}$$

where $C(T)$ and k are the heat capacity of the sample and the thermal leak conductance (assumed constant), respectively, and $s(t)$ is a square wave of unit amplitude, zero average, and period $1/f$.

When, in the steady state,[6]

$$f\tau_1 \gg 1, \tag{6}$$

the average sample temperature is $P_0/2k$, with an oscillatory part T_{ac} which satisfies the equation

$$C\dot{T}_{\mathrm{ac}} = \tfrac{1}{2}P_0 s(t), \tag{7}$$

the fundamental equation of the ac method. For sufficiently small oscillations, C may be assumed constant and (7) integrated to give a triangular wave form of amplitude

$$T_{\mathrm{ac}}{}^0 = P_0/fC. \tag{8}$$

Even in the case of a sample undergoing a first-order transition, (7) remains valid provided that the sample temperature is uniform [i.e., that (4) holds]. The latent heat will then be manifested by a flat portion of the $T(t)$ curve with a duration

$$\Delta t = 2L/P_0. \tag{9}$$

Typical data for a single-crystal sample are shown in Fig. 1. Well above T_{N}, the temperature of the sample in Fig. 1, curve b, has the

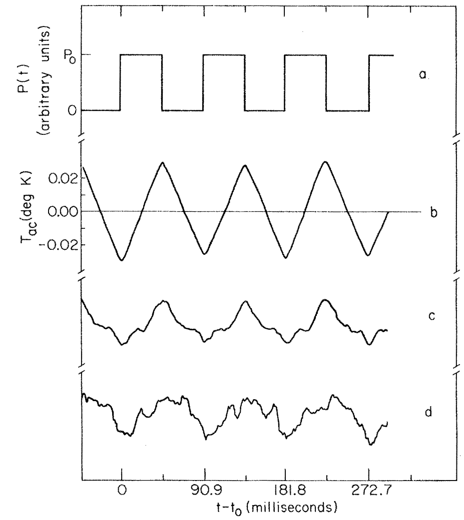

FIG. 1. Temperature oscillations of a Cr sample. a, input heat pulses at $f = 11$ Hz. b, triangular temperature oscillations at $T = T_N + 0.4$ K. c, appearance of a plateau when the temperature oscillations span the first-order hysteresis loop. The curve is the average of sixteen passes. d, single pass spanning T_N. The overshoot and undershoot are due to superheating and supercooling. Hysteresis is apparent on heating and cooling portions of the cycle.

triangular wave form predicted by (8), in phase with the heat pulses in Fig. 1, *a*. Data taken over the frequency range $5 \leq f \leq 200$ Hz show no change in shape, with an amplitude inversely proportional to f, indicating that (4) and (6) are valid. As the temperature is lowered, a plateau appears on both the heating and cooling portions of the cycle, Fig. 1, *c*. Since these curves are the average of sixteen passes, each having the shape of the single pass shown in Fig. 1, *d*, the plateau is smeared. The shape of the single pass shows the effects of superheating, supercooling, and hysteresis on subsequent cycles. The average response in Fig. 1, *c*, may be related to an idealized first-order change as shown in Fig. 2. There, the temperature variation of the sample in the absence of a latent heat is shown as curve *a*. In the case of an idealized first-order transition, with the same specific heat in both phases and no nonequilibrium effects, the average of many passes would have the shape of curve *c*. Because the slope of the heating curve in Fig. 1, *d*, is nearly the same above and below the plateau, the idealized curve which rises to the same temperature as the measured curve, Fig. 2, *b*, will closely approximate the true latent heat. As the amplitude of curve *a* is given by (8), we can easily show that

$$\Delta t = 2C\Delta T/P_0. \tag{10}$$

Substituted into (9), this gives

$$L = C_p\Delta T = 0.19 \pm 0.04 \text{ cal/mole}, \tag{11}$$

where we have used $\Delta T = 34$ mK from Fig. 1, *c*, and the standard value $C_p = 5.70$ cal/mole K near T_N.[7] This result is in good agreement with the estimates (1) and (3) and with the direct measurement of Δt on single passes showing a clear plateau. Our results disagree with those of Sze and Meaden in both the size of L and the presence of a large step in C_p apparent in their data.[3] From Fig. 1, *d*, we may estimate the hysteresis to be on the order of 20 mK.

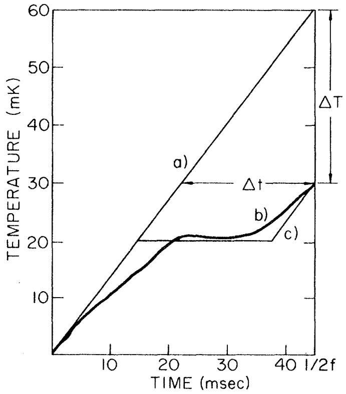

FIG. 2. Schematic representation of Fig. 1. Without a latent heat the temperature rises linearly (curve *a*) with time. In an idealized first-order transition, a plateau is observed (curve *c*). The average of many passes through the transition (curve *b*) rises to the same final temperature as the idealized transition.

The sample used in the measurement was cut from a single crystal supplied by MRC Corp. (99.96%), and then annealed for 80 h above 1000°C, of which 50 h were spent at 1200°C. Unannealed and partially annealed samples (2 h at 1000°C) cut from the same single crystal do not show a latent heat, but a rather weak peak in the specific heat. This is shown in Fig. 3 together with the "specific heat" of the sample showing first-order effects. Annealing decreases the transition temperature and sharpens the peak, a fact which accounts for the wide range of "critical exponents" reported for Cr.[2,8] That the transition is shifted as well as spread seems to indicate that the transition in strained Cr approaches a second-order transition of the BCS type.[9]

The source of the first-order transition is not understood. Kimball[10] has found a first-order transition in a Cr-like model, but with a latent heat of only 0.013 cal/mole, considerably smaller than observed. This model ignores the effective spin-lattice coupling which results from the lattice dependence of the "nesting" area of the electron and hole surfaces. Because this cou-

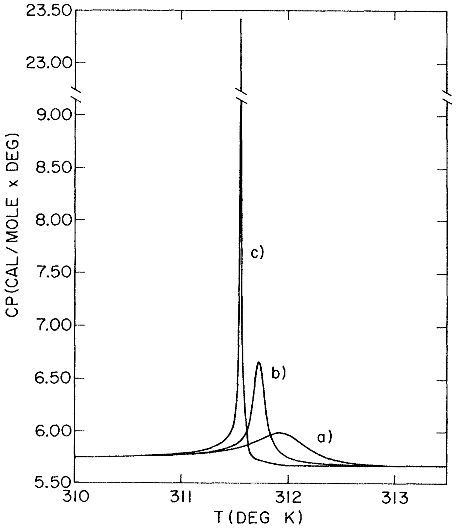

FIG. 3. Specific heat [(first harmonic amplitude)$^{-1}$] of several single-crystal samples. The temperature oscillations were 10 mK. ***a***, unannealed; ***b***, annealed 2 h at 1000°C; ***c***, annealed 80 h above 1000°C and showing a first-order transition.

pling is large (witness the large pressure dependence of the transition temperature[11]) and because the transition is strain dependent, we believe that lattice instability plays an important role. This belief is reinforced by the appearance of the first-order transition below the "strained" second-order transition point which is a feature of the lattice instability model.[12] Clearly, proper allowance for lattice compressibility must be made in the spin-density-wave model[9] before a complete understanding of this unusual phase transition is possible.

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Optical Observation of Stress-Induced Spin Flop in Cr_2O_3*

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It has been observed that applying sufficiently large uniaxial stress to Cr_2O_3 induces in its ${}^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum changes that are nearly identical to those observed when magnetic-field—induced spin flop occurs. This is interpreted as evidence that uniaxial stress induces spin flop in Cr_2O_3. A phenomenological discussion is given.

This Letter reports optical data which constitute strong evidence of uniaxial-stress–induced spin flop in the corundum-structure antiferromagnet Cr_2O_3 ($T_N = 308$°K). Although spin-reorientation phenomena in antiferromagnets and ferrimagnets are well known to occur with the application of magnetic fields or with temperature variations, Cr_2O_3 is the first example of a material in which spin flop can be induced by a uniaxial stress. Experimental evidence of the effect is provided by the observation that uniaxial stress of about 15 kbar applied along the a axis induces in the ${}^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum of Cr_2O_3 fairly abrupt changes that are nearly identical to the changes observed when the spins are forced to flop from the c axis to the basal plane by the application of a c-axis magnetic field exceeding the critical value $H_c = 59$ kG. Qualitative support for the contention of stress-induced spin flop is provided by the observations of Dudko, Eremenko, and Semenenko (DES) that H_c in Cr_2O_3 increases linearly with the magnitude of c-axis uniaxial stress,[1] and that when spin flop is induced with a magnetic field, the crystal spontaneously lengthens along the c axis and contracts perpendicular to the c axis.[2]

The optical absorption spectrum of Cr_2O_3 displays in the vicinity of 7000 Å five reasonably sharp, polarized absorption lines. These are shown in the center trace of Fig. 1 and labeled 1 through 5. Lines 1 and 4 are σ and axially polarized, lines 2 and 3 are π polarized, and line 5 is σ and π polarized. The combinations of lines 1 with 4 and 2 with 3 have been assigned and analyzed in detail by Allen, Macfarlane, and White[3] as pairs of Davydov-split Frenkel excitons associated with single-ion Cr^{3+} transitions from the lowest exchange-split ${}^4A_2$ state to the lowest two exchange-spilt ${}^2E$ states.

Application of a magnetic field along the c axis[4] or of uniaxial stress along the a axis induces changes in the spectrum, some of which are shown in Fig. 1. For small values of stress the lines shift linearly and nearly uniformly to lower