Specific heat of chromium single crystal at temperatures 80-345°K

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The temperature dependence of the specific heat of an iodide chromium crystal is investigated in the 80–345°K range which includes the Neel point ($T_N = 311.4$°K) and the spin-flip temperature ($T_{SF} \approx 124$°K). The $C_P(T)$ curve near T_N reveals a pronounced δ anomaly with hysteresis of less than 0.01 degree, which corresponds to a latent heat of 0.27 ± 0.03 cal/g-atom. The maximum change in energy following magnetic ordering is estimated to be 9.5 ± 1.0 cal/g-atom. The latent heat for a first-order transition at the T_{SF} point is determined for the first time and is $\Delta H_{SF} = (1.70 \pm 0.16) \times 10^{-2}$ cal/g-atom. The hysteresis of the C_P anomaly at the T_{SF} point is ~0.5 deg. An irregularity in the course of the $C_P(T)$ curve is observed in the 220–250°K range which corresponds to the temperature range of redistribution of rhombohedral distortions of the chromium-crystal lattice in the ⟨100⟩ directions. The results are discussed in light of present-day concepts concerning the antiferromagnetism of chromium.

In the most consistent model of the antiferromagnetism of pure Cr, it is assumed that the spin polarization has a sinusoidally-modulated distribution of the type of static spin-density waves along the cubic directions of the bcc lattice[1-3]. The spin waves in Cr are characterized by two types of polarization[4, 5]. In the low-temperature phase (AF_2) the polarization vector **m** is parallel to the wave vector **q**. Above the spin flip temperature (T_{SF} ~ 120°K), in the AF_1 phase, the polarization has cubic directions that are perpendicular to p. The wave vector q of pure Cr is not commensurate with its lattice periods, $q = G(1 - \delta)/2$ (G is the smallest reciprocal lattice vector ⟨100⟩; $\delta \ll 1$ and ranges from ~1/21 to 1/27 when the temperature is varied between 0°K and the Neel point T_N ~ 312°K), whereas in the simple antiferromagnetic phase with localized moments (the AF_0 phase), the period of the magnetic superstructure should be exactly equal to G/2. The magnetic structure of Cr is extremely strongly influence by the impurities, the temperature, the magnetic field, and the external and internal stresses. The oscillatory character of the magnetic structure of pure Cr can be suppressed by doping elements that increase the number of electrons per atom (for example, Mn)[6], and by strong plastic deformation[7]. In either case, the simple antiferromagnetic structure (AF_0 phase) is stabilized.

Thorough neutron-diffraction[4], magnetic[5, 8, 9], and dilatometric[10-13] investigations carried out in recent years offer evidence of a complicated behavior of the thermodynamic properties of Cr on going to the magnetically ordered state ($P \rightarrow AF_1$) and when the symmetry of its magnetic structure is changed ($AF_2 \rightleftarrows AF_1$). It has been established that the symmetry of the Cr lattice changes from cubic to orthorhombic at the Neel point and from orthorhombic to tetragonal at the spin-flip temperature[10]. The finite jumps in the intensity of the neutron scattering[4], and obviously of the specific volume[13, 14] of Cr at the phase-transition temperatures T_N and T_{SF} offer evidence that the two magnetic transitions in pure Cr are of first order. On the other hand, the transition $P \rightleftarrows AF_0$ in doped[6] or strongly deformed[7] pure Cr is a continuous second-order transition.

One of the most reliable criteria of a first-order transition is the presence of a latent heat that can be determined calorimetrically. The latent heat of the $AF_2 \rightleftarrows AF_1$ transition in Cr is exceedingly small and is estimated at ~10^{-4} cal/g[5]. Signs indicating the existence of this heat were revealed by measurement, under steady-state heat flow, of the temperature gradient between fixed points of a long polycrystalline Cr rod under conditions of slow drift of its temperature[15]. So far, no heat of the $AF_2 \rightleftarrows AF_1$ transition in Cr has been observed calorimetrically[16, 17]. Regarding their data on the thermal expansion of Cr single crystals near T_N as a manifestation of a first-order transition, and using the value $dT_N/dP = -5.1 \pm 0.2$ deg/kbar[18], Matsumoto and Mitsui[11] have estimated, using the Clapeyron-Clausius equation, the latent heat of the $AF_1 \rightleftarrows P$ transition at 0.23 ± 0.05 cal/g-atom. The results of measurements of the specific heat of Cr near T_N[17, 19, 20] are in poor agreement with one another. Beaumont et al.[19] observed on the plot of the specific heat of pure (~99.998%) polycrystalline Cr, in the interval 268–324°K, a broad λ anomaly with a jump at 311.5 ± 0.3°K, which they attributed to a second-order phase transition. According to their data, the jump of the specific heat at the Neel point of Cr amounts to ~0.15 cal/g-atom-deg, the total change of the energy for the λ anomaly is $\Delta H_t = 1.4$ cal/g-atom, and the total change of the entropy is $\Delta S_t = 4.4 \times 10^{-3}$ cal/g-atom-deg. In[17], where both single-crystal and polycrystalline samples were investigated, the change of the entropy due to the transition of Cr to a magnetically ordered state is estimated at ~7×10^{-3} cal/g-atom-deg. The authors of the two cited papers[17, 19] obtained no information on the latent heat of the $AF_1 \rightleftarrows P$ transition. Sze and Meaden[20] estimated the latent heat ΔH_{TN} from the value of the "plateau" on the cooling thermogram of pure polycrystalline Cr, as recorded with an adiabatic calorimeter. The value obtained by them ($\Delta H_{TN} = 0.47 \pm 0.10$ cal/g-atom) should be regarded as the upper limit of the possible values of ΔH_{TN}.

Garnier and Salamon[21] determined ΔH_{TN} in well-annealed Cr single crystals (0.19 ± 0.04 cal/g-atom) with the aid of a high-sensitivity modulation calorimeter. The method used by Garnier and Salamon is relative, and therefore, when plotting the excess specific heat near T_N, these authors were forced to use "base" values of $C_P(T)$ taken from[19]. It is obvious that Garnier and Salamon could not obtain detailed information on the behavior of the specific heat of the Cr single crystals in a temperature interval not directly adjacent to T_N, nor could they obtain information on the jump of the specific heat and the ratio of the latent heat to the total energy of the ordering process. Weber and Street[22] recently carried out a very careful investigation of the specific heat of well-annealed Cr polycrystals in the interval 280–330°K, using an adiabatic method with controlled heating. Near the temperature 311.6 ± 0.5°K they succeeded in separating the δ-singularity of the specific heat, from which they determined the latent heat, $0.15\ \text{cal/g-atom} \le \Delta H_{T_N} \le 0.25$ cal/g-atom. The total change of the energy and entropy following the magnetic ordering of Cr is estimated in[22] at $\Delta H_t = 5$ to 918 cal/g-atom and $\Delta S_t = (16.7–32.7) \times \times 10^{-3}$ cal/g-atom-deg, values much higher than the results of earlier studies[17, 19].

The investigation undertaken by us was aimed at obtaining direct data on the thermodynamic characteristics of the transition $AF_1 \rightleftarrows P$ in pure and perfect Cr crystals, at an investigation of the temperature dependence of the specific heat of such crystals in the magnetically ordered state, and at a search for the latent heat of the transition $AF_2 \rightleftarrows AF_1$ and the relaxation effects due to the magnetic domain structure.

PROCEDURE AND EXPERIMENTAL RESULTS

The principal measurements were made on an iodide Cr single crystal of arbitrary orientation, having a purity 99.996% and a resistance ratio R(300°K)/R(4.2°K) ≈ 250. The mass of this crystal was 290 mg. The specific heat near T_N was investigated also with a single crystal of 1.5 g mass, cut from a large-grain crystal obtained by argon-arc remelting of electrolytic chromium of ~99.95% purity. After vacuum annealing (1250°C, 50 hours) and slow cooling, the resistance ratio of this sample was ~100. In addition, we investigated a polycrystalline sample (2.5 g) prepared from high-purity (99.995%) chromium. The resistance ratio for the polycrystal was close to 25. A microcalorimetric method with monotonic heating (cooling) was used to measure the specific heat. This method had a high temperature resolution and a sensitivity up to 1×10^{-7} W. The justification of the method, the calculation formulas, and the construction of the calorimeter for the 80–300°K range were published earlier[23].

A four-channel differential microcalorimeter, adapted to operate under both cooling and heating conditions[24] was used for the measurements above room temperature. In the calculation of the specific heat, account was taken of the possible inequality of the temperature drifts of the sample and of the calorimetric envelope[23]. The corrections connected with this circumstance are most significant when the phase transition point is approached, in view of the increase of the specific heat dC/dT. The error in the absolute determinations of the specific heat did not exceed 3%. The accuracy with which the transition temperatures were determined was limited by the possible "non-isothermy" of the crystals. At the employed rates of change of the temperature (≤ 10 deg/hr), the "non-isothermy" of the samples under the experimental conditions (the temperature drop between the surface and the center) did not exceed 0.01 deg.

Figure 1 shows the results of measurements of the specific heat of three different Cr samples in the immediate vicinity of the Neel point, with curve 1 pertaining to the iodide single crystal, 2 to the cast single crystal, and 3 to the polycrystal. All curves of Fig. 1 were obtained with the temperature rising at a rate of 0.8 deg/hr. To exclude random errors, each temperature curve was plotted no fewer than five or six times. Figure 1 shows the average values of these measurements1). The distinct δ anomaly of the specific heat near T_N that is customarily attributed to the latent heat of the first-order transition, can be distinguished only in the case of the iodide crystal (curve 1). On going to the less perfect cast crystal (curve 2), the symmetry of the specific-heat anomaly is violated, and its height decreases. In the polycrystalline sample (curve 3), the anomaly of C_p resembles the smeared-out λ anomaly of continuous transitions. It is obvious that when the quality of the samples becomes worse, the effective transition "point" determined from the maximum of the specific-heat anomaly or from the largest slope of this anomaly on the high-temperature side increases. The shift of the effective Neel "point", together with the change of the character of the anomaly of the specific heat in the immediate vicinity of this "point", was observed earlier[21] for Cr single crystals subjected to different heat treatments.

Figure 2 illustrates the change in form of the anomaly of the specific heat of the iodide crystal as a function of the direction of the change of the temperature on going through the Neel point (311.4°K): namely, curve 1–heating at a rate 0.8 deg/hr, curve 2–cooling at the same rate. The use of the indicated temperature drift rate does not lead to noticeable effects of overheating or overcooling, from which we conclude that the hysteresis of the first-order transition in the iodide crystal does not exceed the absolute error with which the sample temperature is determined (~0.01 deg). A similar conclusion with respect to the value of the temperature hysteresis at the Neel point of Cr was arrived at by Garnier and Salamon[21]. Attention is called to the circumstance that the anomaly of the specific heat is sharper in the $P \rightarrow AF_1$ transition (the width of the anomaly at half height does not exceed 0.1 deg) than in the $AF_1 \rightarrow P$ transition (Transition width ~0.15 deg). The latent heat, calculated as the integral under the plot of the δ anomaly of the specific heat, is the same in cooling and in heating, and amounts to 0.27 ∓ 0.03 cal/g-atom. The estimated error in the calculation of ΔH_{T_N} is due

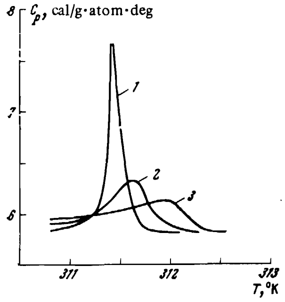

FIG. 1

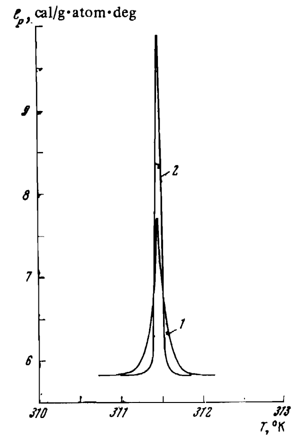

FIG. 2

FIG. 1. Specific heats of three samples of chromium in the immediate vicinity of the Neel point: 1–iodide single crystal; 2–cast single crystal, 3–polycrystal.

FIG. 2. Specific heat of iodide crystal near the Neel point: 1–heating at rate 0.8 deg/hr; 2–cooling at the same rate.

to the uncertainty in the values of the heat-exchange coefficients, which were determined by calibration[23], to the leeway in the determination of the integration limits, and to the inaccuracy of the graphic integration itself.

The character of the correlation between the δ anomaly and the temperature dependence of the specific heat above and below the Neel point is illustrated in Fig. 3, which shows the temperature dependence of the specific heat of the iodide crystal in the interval 150–345°K. It is obvious from this figure that the "magnetic" contribution to the specific heat of Cr is not limited to the δ anomaly of the first-order transition, but is manifest in the same manner as the broad anomaly (270–340°K), which is asymmetrical about the transition point. Outside the limits of the "magnetic" anomaly, the temperature dependence of the specific heat of the single crystal agrees in the main with the measurement results[16, 19, 22] obtained with polycrystalline samples. It is of interest to estimate the total contributions of the magnetic ordering to the energy and entropy of the Cr. The numerical values of these quantities can depend strongly on the choice of the nonsingular part of the specific heat. The simplest approximation used to determine the "base line is[17, 19, 22] extrapolation of the measured values of C_P from the low-temperature and high-temperature sides. Weber and Street[22] also estimated the upper limits of the changes in the energy and entropy in the magnetic ordering of Cr using "base" line in the form of the sum of the Debye contribution C_g and the linear electronic contribution γT with allowance for the difference $C_P - C_V = AC_P^2T$ (γ is the coefficient of the electronic specific heat, and A is the Gruneisen constant). The inaccuracy of the analysis[22] is due to the unjustified use, for Cr, of a linear temperature dependence of the specific heat near T_N. It is known that the electronic specific heat of Cr has a nonlinear behavior both below[25] and above[26] the Neel point and appears to make an appreciable contribution to the observed "magnetic" anomaly.

The electronic specific heat of chromium $C_e = C_V - C_g$ in the temperature interval 150–345°K is plotted in Fig. 4. In the calculation of $C_e(T)$ we followed the procedure proposed by Goff[26]. We used the $C_g(T)$ curve calculated by Feldman[27] on the basis of an analysis of the results of a neutron-diffraction investigation of the phonon spectrum of Cr; this curve agreed well with the $C_g(T)$ curve obtained in a measurement of the low-temperature specific heat[16]. The Gruneisen constant was assumed equal to 2.78×10^{-6} cal^{-1} [26]. Curve 1 of Fig. 4 is a plot of the C_e of chromium, and was obtained on the basis of our present results, while curve 2 is a linear approximation obtained for C_e with the aid of estimates[25] of the values of γ for the antiferromagnetic and paramagnetic phases. It is obvious from Fig. 4 that the temperature dependence of the electronic specific heat of chromium differs significantly from the behavior expected for normal metals with a degenerate electron "gas." Extrapolating the specific heat of the paramagnetic phase C_{eP} to lower temperatures (curve 3 of Fig. 4) we find that $C_{eP} \approx C_{eA}$ near 180°K. The difference between the entropies of the two phases at this temperature is $(29 \pm 3) \times 10^{-3}$ cal/g-atom-deg, and the energy difference is (9.5 ± 1) cal/g-atom. The error in the values of ΔS_t and ΔH_t calculated in this manner is due mainly to the leeway in the extrapolation of the C_{dP} curve to lower temperatures.

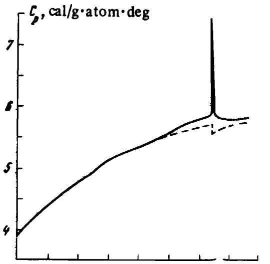

FIG. 3

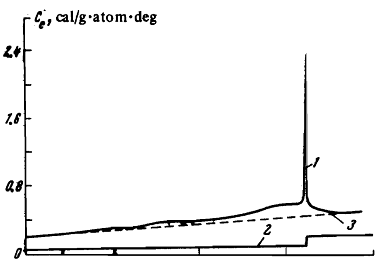

FIG. 4

FIG. 3. Specific heat of iodide crystal in the temperature interval 150–345°K (solid curve); theoretical curve for the specific heat of Cr near the Neel point [27] (dashed).

FIG. 4. Electronic specific heat of chromium $C_e = C_V - C_g$ (C_g is the specific heat of the lattice in the Debye approximation): 1—values of C_e calculated on the basis of the results of the present paper (Fig. 3); 2—linear approximation for C_e; 3—extrapolated specific heat C_{eP} of the paramagnetic phase.

The wave-like irregularity of the temperature dependence of the specific heat observed in Figs. 3 and 4 in the interval 220–250°K exceeds the limits of random errors. Regular deviations of the experimental points from the smoothed specific-heat curve can be observed in the same temperature interval in the measurement results of Clusius and Franzosini[16].

The temperature variation of the specific heat of Cr in the interval 80–150°K is shown in Fig. 5. The values of $C_P(T)$ shown in Fig. 5 agree with the results of earlier investigations, with the exception of a narrow temperature region (123–126°K) in which we succeeded in observing an exceedingly weak δ-anomaly of the specific heat, pertaining to the phase transition $AF_2 \rightleftarrows AF_1$. To determine this anomaly, the differential cells of the calorimeter[23] were carefully "balanced" with respect to the time constant (by selecting the standard) and with respect to the sensitivity (by electrical shunting). Under the conditions of the obtained "thermal symmetry," the resolution of the instrument was limited by the thermal-noise level and was no worse than 1×10^{-7} W. The thermal effects connected with the $AF_2 \rightleftarrows AF_1$ transition could be observed only for the most perfect iodide crystal. These effects are represented in the form of anomalies of the specific heat in the lower right corner of Fig. 5 (curve a corresponds to cooling at a rate 1 deg/hr, and curve b to heating at the same rate). The basic values of the specific heat were determined from the smoothed $C_P(T)$ curve (upper part of Fig. 5) obtained in preliminary experiments. The hysteresis of the anomaly of the specific heat, due to the $AF_2 \rightleftarrows AF_1$ transition, is approximately 0.5 deg. The width of the transition does not exceed ~1 deg, in agreement with the neutron-diffraction observations made on perfect

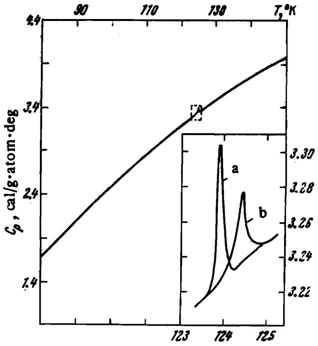

FIG. 5. Specific heat of iodide crystal in the temperature interval 80–150°K. In the lower-right corner is shown the anomaly of the specific heat due to the phase transition $AF_2 \rightleftarrows AF_1$: curve 1—cooling at rate 1 deg/hr; curve b—heating at the same rate.

single crystals[4]. The latent heat of this transition ΔH_{TSF} is estimated at $(1.7 \pm 0.16) \times 10^{-2}$ cal/g-atom or $(3.2 \pm 0.3) \times 10^{-4}$ cal/g, and the change of the entropy ΔS_{TSF} at the average transition temperature 124.1°K is estimated at $(1.36 \pm 0.14) \times 10^{-4}$ cal/g-atom-deg. Just as in the case of the $AF_1 \rightleftarrows P$ transition, the spreading of the δ anomaly of the specific heat for the $AF_2 \rightleftarrows AF_1$ transition is somewhat larger in heating than cooling.

The thermodynamic characteristics of the phase transitions in chromium, obtained in the present paper, are compared in Tables I and II with the corresponding values measured and calculated by others.

DISCUSSION OF RESULTS

According to the prevailing notions, the antiferromagnetic structure of Cr is the result of instability of the system of 3d(4s) electrons with respect to a transition to a state with "spin-density wave"[1-3]. It is assumed[1-3, 28] that the decisive influence on the stabilization of the modulated magnetic structure of Cr is exerted by the special properties of the electronic energy spectrum of this metal, namely the presence of broad and almost flat (electron and hole) regions of the Fermi surface, which ensure an appreciable logarithmic singularity for translations close to the wave vector of the magnetic structure **q**. Weighty arguments favoring the electronic nature of the antiferromagnetism of Cr are the absence of disordered magnetic moments (paramagnetic neutron scattering) above the Neel point[29] and the excessively weak anomaly of the specific heat at this point. The change of the entropy following magnetic ordering of Cr (29.0×10^{-3} cal/g-atom-deg) is much lower than the value $(1/2)R \ln 2 \approx 0.7$ cal/g-atom-deg expected for the $P \rightarrow AF$ transition in the model of localized atomic moments[3]. It appears that chromium is the only transition metal in which the thermal vanishing of the magnetism is due to single-electron excitations, namely the suppression of the moments by the temperature transfers of the spins through the energy gap that is produced at 0°K[2].

TABLE I. Thermodynamic characteristics of paramagnetism—antiferromagnetism phase transition

ΔH_t, cal/g·atom	$\Delta S_t \cdot 10^3$, cal/g·atom·deg	ΔH_{T_N}, cal/g·atom	$(\Delta V/V)_{T_N} \cdot 10^6$, %	Remarks
9.5 ± 1.0	29 ± 3	0.27 ± 0.03	8.0 ± 1.3	Present paper, $(\Delta V/V)_{TN}$ calculated from the Clapeyron-Clausius formula
.5—9.8	16.7 ± 32.7	0.15—0.25		[22]
		0.19 ± 0.04		[21]
		0.47 ± 0.10		[20]
	7 ± 0.5			[17]
1,4	4.4			[19]
		0.23 ± 0.05		Calculated from the Clapeyron-Clausius equation [11]

TABLE II. Thermodynamic characteristics of the phase transition at the spin-flip points

$\Delta H_{T_{SF}} \cdot 10^2$, cal/g·atom	$\Delta S_{T_{SF}} \cdot 10^4$, cal/g·atom·deg	$(\Delta V/V)_{T_{SF}} \cdot 10^6$, %	Remarks
1.70 ± 0.16	1.36 ± 0.14	4.10 ± 0.15	Present paper, $(\Delta V/V)_{TSF}$ calculated from the Clapeyron-Clausius equation
	0.50		Calculated on the basis of magnetic measurements [5]
		1.4 ± 0.6	[10]
		~ 300	[14]

Many properties of antiferromagnetic Cr can be adequately explained by the theory of spin-density waves[3, 30, 31]. The spin-wave state is treated as the ground state of a system of collectivized electrons, obtained in the self-consistent-field approximation. The theoretical calculations of the spin-wave structure are made difficult, however, by the lack of exact data on the form of the Fermi surface of the metal. The use of the simplest two-band model with electron and hole bands of equal dimensions leads to the following results[30]: The $P \rightarrow AF$ transition should be of second order, analogous to the transition from the normal to the superconducting state in the Bardeen-Cooper-Schrieffer (BCS) theory. This theory predicts a finite jump of the electronic specific heat at the Neel point, owing to the appearance of an energy gap of the BCS type and to the change of the effective topology of the Fermi surface. The connection between the $P \rightarrow AF$ Transition and the decrease of the electronic contribution to the specific heat was established by Heiniger and co-workers[25] on the basis of an investigation of the low-temperature specific heat of Cr and its alloys. Extrapolating the values of the coefficients of the electronic specific heat $\gamma_P(0)$ of paramagnetic Cr alloys to zero concentration, Heiniger et al.[25] estimated the value of $\gamma_P(0)$ for pure paramagnetic Cr at 6.9×10^{-4} cal/g-atom-deg^2. The average value of the coefficient $\gamma_A(0)$ of antiferromagnetic Cr, according to data by various authors, is 3.6×10^{-4} cal/g-atom-deg^2 [25]. Using the expression of the BCS theory[32], $\Delta C/\gamma' T_N = 1.43$ for the jump of the specific heat at the Neel point of Cr, where $\gamma' = \gamma_P(0) - \gamma_A(0)$ is a quantity analogous to the Sommerfeld coefficient at 0°K for the electrons in the normal state and T_N is analogous to the critical temperature of the transition to the superconducting state, and neglecting the temperature dependences of γ_A and γ_P, we obtain $\Delta C \sim 0.11$ cal/g-atom-deg, which is fair agreement with the experimental value (~ 0.16 cal/g-atom-deg). From the results of Heiniger et al.[25] it follows that the Fermi surface of Cr is reduced by a factor of two on going to the antiferromagnetic state, $N_P/N_A \approx \gamma_P(0)/\gamma_A(0) \approx 2$, where N_P and N_A are the densities of the electronic states at the Fermi level in the paramagnetic and antiferromagnetic phases. This conclusion agrees qualitatively with the appreciable decrease of the electric conductivity (by approximately 30%)[33] and of the magnetic susceptibility[8] of Cr in the transition $P \rightarrow AF$.

The dashed curve of Fig. 3 shows the temperature dependence of the specific heat of Cr in the vicinity of T_N, as calculated by Feldman[27] using the data of Heiniger et al.[25] and the values of the BCS electronic specific heat tabulated by Muhlschlegel[32]. On the basis of the experimental data on the spin-wave spectrum of Cr and its alloys, Feldman has concluded that the spin-wave excitations make a negligible small contribution to the specific heat at temperatures close to T_N. The contribution of the lattice to the specific heat was calculated[27] in the harmonic approximation on the basis of the Born-Karman analysis of the results of an investigation of the Phonon spectrum of Cr[34]. The possible change of the phonon spectrum as a result of the change of the electronic structure at the Neel point was disregarded in this case. The corrections for the anharmonicity, calculated using the data of Sully and Brandes[35] on the compressibility and thermal expansion of Cr, did not exceed 1%. It is obvious from Fig. 3 that the theoretical $C_P(T)$ curve does not describe the detailed behavior of the specific heat of Cr in the vicinity of T_N. This is due principally to the fact that the electronic model used in Feldman's calculation[27] regards the P → AF transition as a second-order transition, whereas actually this is a weak first-order transition close to the critical point of the second-order transitions.

There is still no satisfactory microscopic theory of phase transitions in Cr. Attempts at theoretically demonstrating the feasibility of a first-order transition from the paramagnetic to the spin-wave state were undertaken in[31, 36-38]. Using a model with two bands that are produced by hybridization of the band of the free electrons and the band of the strongly bound electrons, Kimball and Falikov[31] have shown that the transition from the paramagnetic to the spin-wave state, calculated in the self-consistent-field approximation, should be of first order at all finite temperatures. However, the latent heat of such a transition in Cr, as predicted by the theory of Kimball and Falikov[31] ($\sim 1.2 \times 10^{-2}$ cal/g-atom), is much lower than that obtained in experiment. The main cause of the poor agreement of the Kimball and Falikov theory with experiment is obviously that the Hartree-Fock approximation that they used to solve the problem of the appearance of spin-density waves in Cr is not valid[28].

In[36-38], the problem of the character of the Cr transition to a state with spin-density wave is solved in a semiphenomenological approximation on the basis of the Landau theory, which regards the thermodynamic state of the system as a function of the order parameter–the average spin density $n \equiv \langle n(\mathbf{r})\rangle$. In the vicinity of T_N, the free energy of the system is represented as an expansion in powers of n:

$$F=b_1n^2+{}^1/_2b_3n^4+{}^1/_3b_5n^6+\dots \tag{1}$$

The coefficients b_1, b_3, and b_5 of the expansion (1) are estimated by starting with a two-band model of a metal whose Fermi surface contains spherical electron and hole sections with different diameters[38]. In this model, the problem of the transition of the metal into a state with a spin-density wave is similar to the problem of the transition of a weak ferromagnet into an inhomogeneous superconducting state[39]. Nakanishi and Maki have shown[38] that in the vicinity of the triple point, where paramagnetic, modulated antiferromagnetic (AF_1) and simple antiferromagnetic (AF_0) phases coexist for a sinusoidal spin-density wave, $n(\mathbf{r}) = 2^{1/2}n(\mathbf{q})\sin(\mathbf{qr})$, the conditions needed in order for the P → AF_1 transition to be of first order may be realized in the employed model, namely $b_1 > 0$, $b_3 < 0$ and $b_5 > 0$. To the contrary, the P → AF_0 transition should be of second order in this model. The theory of Nakanishi and Maki[38], in spite of its rather approximate character, predicts values for the latent heat and for the jump of the specific heat (~0.24 cal/g-atom and ~0.1 cal/g-atom-deg, respectively) that agree fairly well with experiment[2]. In the calculations of Nakanishi and Maki[38] no account was taken of the influence of the spin-lattice interaction (magnetostriction) on the order of the phase transition at the Neel point. The presence of this interaction can be postulated because of the strong dependence of the antiferromagnetic state of Cr on the volume[33] and uniaxial[5] deformations. In the opinion of Malaspinas and Rice[37], the striction effects in Cr are not strong enough to favor a first-order phase transition (AF ⇄ P) by the mechanism of Bean and Rodbell[41].

In the elastic-isotropic model of a solid, allowance for the lattice compressibility and for the interaction with the acoustic phonons leads to a first-order transition in the case when the specific heat becomes infinite without allowance for the acoustic effects at the critical point of the second-order transitions[42]. Such a transition should be preceded by loss of the absolute stability of the compressed lattice. The physical consequence of this fact is the existence of a temperature interval in which the Poisson coefficient ν becomes negative[42]. At these temperatures, any unilateral tension causes an isotropic expansion of the sample. For Cr, the possibility of lowering the coefficient ν near T_N to negative values was demonstrated by Pursey[43]. The condition for the realization of a first-order transition close to the critical point is the relation[42]

$$[4G_0K_0(dT_N/dP)^2\Delta C_P]/[T_N(3K_0+4G_0)]>1, \tag{2}$$

where dT_N/dP is the baric coefficient of the transition point, K_0 and G_0 are the nonsingular parts of the hydrostatic-compression and shear moduli, and ΔC_P is the anomalous part of the specific heat per unit volume (with allowance for the correlation effects). Using for Cr the values $G_0 \approx 1.2 \times 10^{12}$ dyn/cm^2, $K_0 \approx 1.6 \times 10^{12}$ dyn/cm^2[38], and $dT_N/dP = -5.1$ deg/kbar[18], as well as the values of ΔC_P obtained by us and by Weber and Street[22], it can easily be shown that the condition (2) is not satisfied for chromium. Thus, the first-order phase transition and the experimentally-observed negative Poisson coefficient[43] of Cr cannot be attributed to loss of stability of the compressed lattice near the critical point[42].

Shimizu[44] has anlayzed the thermodynamic properties of the spin-wave states of Cr (AF_1 and AF_2) in detail on the basis of the band theory of magnetism. He used the model of a metal with two parabolic bands, on the basis of which he obtained a phenomenological expression for the energy change due to the modulated distribution of the spin density $n(\mathbf{r})$. According to Shimizu, the conditions ($b_1 > 0$, $B_3 < 0$, and $b_5 > 0$) for realization of the first-order phase transition P → AF agree with the estimate of the coefficients b_1, b_3, and b_5 from the energy-band scheme of the Cr structure, as calculated by Asano and Yamashita[40]. The numerical values of the coefficients were obtained by Shimizu[44] by comparing the calculated values of n^2 with those observed by Arrott et al.[4] at 0°K and T_N. In addition, in accord with the data of Heiniger et al.[25], it was assumed that $\Delta C/T$ at 0°K is equal to $\gamma_A(0) - \gamma_P(0) = -3.59 \cdot 10^{-4}$ cal/g-atom-deg^2. The temperature dependences of the thermodynamic properties of the spin-wave state of Cr relative to its paramagnetic state, obtained on the basis of the Shimizu theory, are shown in Fig. 6 (ΔC is the specific heat, ΔS is the entropy, ΔU is the internal energy, and ΔF is the free energy). The plots of the differences of the thermodynamic properties of the spin-wave and paramagnetic states of chromium against the temperature (with the exception of the behavior near T_N) recall the plots of the analogous quantities for the superconducting and normal phases[45]. The differences of the entropies and energies of the two phases go through a maximum at a certain temperature below T_N and at the same temperature (~160°K) we have $C_{eP} = C_{eA}$. The maximum values predicted by the Shimizu theory[44] for the differences of the entropy and the energy ($\Delta S = |S_A - S_P| \sim 37 \cdot 10^{-3}$ cal/g-atom-deg and $\Delta U = |U_A - U_P| = 9.2$ cal/g-atom) are in fair agreement with

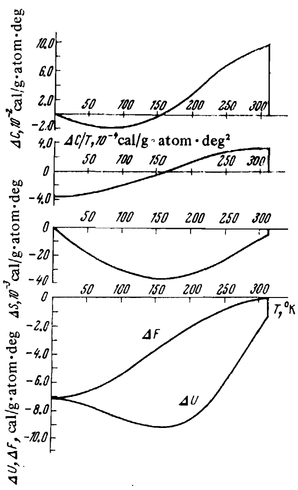

FIG. 6. Temperature dependence of the specific heat (ΔC), ΔC/T, the entropy ΔS, the internal energy ΔU, and the free energy ΔF of the spin-wave state of chromium, calculated on the basis of the Shimizu theory [44].

the experimental values $\Delta S_t = (29 \pm 3) \cdot 10^{-3}$ cal/g-atom-deg and $\Delta H_t = 9.5 \pm 1.0$ cal/g-atom. The theory predicts for the latent heat and for the jump of the specific heat at the Neel point the values ~1.4 cal/g-atom and ~0.1 cal/g-atom-deg.

Assuming, in qualitative agreement with the experimental observations[4], that the amplitude n and the wave vector **q** of the spin waves experience no jumplike changes at the point T_{SF}, Shimizu[44] expressed the difference of the free energies of the AF_1 and AF_2 phases near T_{SF} in the form

$$\Delta F = \Delta F_{AF_2} - \Delta F_{AF_1} = {}^3/_8 q^2 n^2 \Delta E, \tag{3}$$

where ΔE is positive at $T > T_{SF}$, vanishes at the point T_{SF}, and is negative at $T < T_{SF}$. In the approximation used by Shimizu, the $AF_2 \rightleftarrows AF_1$ transition should not be accompanied by a jump of the entropy thus contradicting our results.

The excess entropy of the AF_1 phase relative to the phase AF_2 is exceedingly small at the point T_{SF} (~1.36×10^{-4} cal/g-atom-deg). Street et al.[5] estimated this quantity from data on the lowering of the T_{SF} point of a polycrystalline Cr sample by an external magnetic field H_m applied in the same direction as the field H_c ~ 80 kG in which the sample was cooled beforehand through the Neel point. It was assumed that the procedure of cooling in the magnetic field contributed to obtaining a "single-**q**" state, for which the jump of the magnetic susceptibility $\chi^q_{AF_1} - \chi^q_{AF_2} \approx 1.6 \cdot 10^{-7}$ emu/g, measured along the direction of the vector **q**, was observed in[8] at the point T_{SF}. Neglecting the change of the internal energy and of the volume of the metal due to application of the external field, Street et al.[5] expressed the entropy of the $AF_2 \rightleftarrows AF_1$ transition in the form

$$\Delta S_{TSF} \approx {}^1/_2 (\chi^q_{AF_1} - \chi^q_{AF_2}) (dH_t/dT) H_t, \tag{4}$$

where H_t is the critical field of the transition, which was approximated in a limited temperature interval3) (95°K–T_{SF}) by the equation $H_t^2 = H_0^2(1 - T/T_{SF})$, $H_0 = 260$ kG, $T_{SF} \approx 123.5$°K. Using Eq. (4), Street et al. obtained $\Delta S_{TSF} \approx 0.5 \times 10^{-4}$ cal/g-atom-deg. Taking into account the assumptions made in the derivation of Eq. (4) and the possible imperfection of the "single-q" state of the polycrystalline samples investigated in[5], one can regard the estimates of ΔS_{TSF} on the basis of the magnetic measurements to be in satisfactory agreement with the calorimetric results.

The latent heat $\Delta H_{TN} = 0.27 \pm 0.03$ cal/g-atom obtained by us corresponds to a specific-volume jump $(\Delta V/V)_{TN} = (8.0 \pm 1.3) \cdot 10^{-6}$, which is evidence of the appearance of a noticeable volume magnetostriction at the Neel point of Cr. In the estimate of $(\Delta V/V)_{TN}$ we used the values $dT_N/dP = -5.3 \pm 0.3$ deg/kbar[18] and $V_{TN} = 7.22$ cm³/g-atom[13]. Investigations of the magnetostriction and of the thermal expansion of Cr single crystals in the "single-**q**" state have shown[10] that the relative increase of the Cr lattice parameter on going to the antiferromagnetic state is

$$(\delta l/l)_q > (\delta l/l)_h > (\delta l/l)_m \text{ between } T_N \text{ and } 230° \text{ K}$$
$$(\delta l/l)_h > (\delta l/l)_m > (\delta l/l)_q \text{ between } 230° \text{ K and } T_{SF} \text{ and}$$
$$(\delta l/l) > (\delta l/l)_{m,q} \text{ below } T_{SF}$$

(the symbols q, h, and m designate the ⟨100⟩ axes that coincide with the direction of the wave vector **q**, the magnetization **m**, and the normal to them **h**). The relative changes of the Cr lattice parameters amount to 10^{-5}–10^{-6} [10] and are beyond the sensitivity of the x-ray-diffraction method[4]. Tetragonal distortions of the Cr lattice were noted, however, in investigations of the electron diffraction[46] and of the de Haas–van Alphen effect[47]. According to Steinitz et al.[10], in addition to a change in the symmetry of the Cr lattice from orthorhombic to tetragonal, an isotropic increase of the volume, $(\Delta V/V)_{TSF} \approx (1.4 \pm 0.6) \cdot 10^{-6}$, takes place in the $AF_1 \rightarrow AF_2$ transition. Using the experimental values $dT_{SF}/dP = -5.8 \pm 0.2$ deg-kbar[48], $V_{TSF} = 7.2$ cm³/g-atom[13], and $\Delta S_{TSF} = (1.36 \pm 0.14) \cdot 10^{-4}$ cal/g-atom-deg (our results) we obtain from the Clapeyron-Clausius equation $(\Delta V/V)_{TSF} = (4.10 \pm 0.15) \cdot 10^{-6}$. Taking into account the measurement errors due to the slightness of the effects and the possible imperfection of the "single-q" state of the crystals investigated in[10]4), the agreement of the two methods of estimating $(\Delta V/V)_{TSF}$ is not bad.

The value $(\Delta V/V)_{TSF} \sim 3 \cdot 10^{-4}$, which follows from the results of the measurement of the lattice parameters of polycrystalline Cr[14], exceeds by two orders of magnitude the values obtained by us and by Steinitz et al.[10]. In the Temperature interval T_N–T_{SF}, perfect Cr crystals apparently contain equal numbers of domains with six orientations $(q_i m_j)_{i \neq j}$, where i, j = 1, 2, 3 pertain to the cubic axes of the crystal. The average volume of the domains at 129°K is estimated at $(2.8–4.4) \times 10^{-16}$ cm³ [9]. At the point T_{SF} the crystal goes over into an AF_2 state with three types of domains $(q_i m_i)$. If the temperature is varied cyclically in the interval T_N–T_{SF}, the redistribution of the sample volume among the domains with different modulation vectors of the spin density leads to the appearance of a temperature hysteresis of the magnetic neutron-diffraction reflections[4,49]. At constant temperature, the changes in the magnetic structure of Cr fluctuate[49]. It is assumed[4,49] that the two indicated phenomena are due to a redistribution of the internal stresses that are produced by the presence of the antiferromagnetic domains. In Cr crystals that are not sufficiently well purified to eliminate interstitial impurities, one can note near T_N a slow relaxation (with time constant 10^4–10^5 sec) of the lattice parameters and of the resistivity, which is attributed to the diffusion redistribution of the impurities in the internal-stress field[50]. In an investigation of the specific heat of Cr polycrystals by the adiabatic method of stepwise heating[22], the relaxation effects appeared after maintaining the samples at a temperature close to T_N for several hours. In our experiments, these effects were not observed. This circumstance can be attributed both to the peculiarities of the calorimetric method employed by us, and to the sufficiently high purity of the investigated crystal.

The temperature interval noted in Fig. 3 (220–250°K), in which the specific heat has an irregular behavior, agrees with the temperature region in which the rhombohedral distortions of the Cr lattice are redistributed among the directions of **q**, **m**, and **h**[10]. It appears that this circumstance is not accidental, and gives grounds for attributing the irregularity of the $C_P(T)$ curve to thermoelastic effects due to the changes in the internal strains. Observation of these effects offers evidence that the magnetic structure of the investigated Cr sample has a multidomain character, such that independent variation of the shapes of the individual domains is excluded. The difference between the microstructure (domain) state of Cr on opposite sides of the points of the phase transitions $AF_1 \rightleftarrows P$ and $AF_2 \rightleftarrows AF_1$ seems to determine the observed differences in the broadening of the δ anomalies of the specific heat when the temperature is raised and lowered.

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1) The heat-capacity curves, $C_P(T)$, were calculated from thermograms recorded with an automatic recording potentiometer. Thus the "experimental points," whose density can be as high as one pleases in our method, are not shown in Fig. 1 or subsequent figures.

2) Nakanishi and Maki [38] indicated in error a value 0.74 cal/g-atom for the latent heat ΔH_{TN}. Our values of ΔH_{TN} and ΔC were obtained in Fig. 6 of [38] and the following values of the parameters: $T_{N0} \approx 700$°K, $N(0) \approx 3.5\ Ry^{-1}$ (1 Ry = 13.6 eV). Here N(0) is the density of states on the "magnetic" part of the Fermi surface of Cr [40] and T_{N0} is the Neel point for the $P \rightarrow AF_0$ phase transition under the condition that the diameters of the electron and hole Fermi surfaces are equal. The last condition appears to be realized in Cr-Mn alloys [6].

3) Below 90°K, the process of the reversible shift of the point T_{SF} by an external field gives way to an irreversible transfer of the modulation vector **q** to a direction perpendicular to the field H_m [5].

4) The method used in [5,10] to obtain the "single-**q**" state of the Cr crystals does not exclude the possibility of the presence of domains with "random" modulation vectors [49].

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