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Heat-capacity studies of chromium-rich antiferromagnetic chromium-iron alloys

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The specific heats of polycrystalline Cr and Cr alloys containing 2.3-, 3.3-, and 4.9-at.% Fe have been measured with a differential calorimeter in a temperature range around the Néel point. Our results are in general agreement with the recent specific-heat measurements by Suzuki. However, the Cr–3.3-at.%-Fe sample is found to exhibit a peculiar avalanche effect which we attribute to a nucleation-controlled phase transition from a metastable magnetic state. Such an interpretation is consistent with Suzuki's results for Cr containing 3.0- and 4.0-at.% Fe, suggesting that the avalanche effect may extend over this entire compositional region.

I. INTRODUCTION

When Fe is dissolved in the Cr lattice, it is possible, depending upon the Fe concentration, to obtain three magnetic phases: (i) paramagnetic (P): (ii) incommensurate (either transverse spin density wave AF(1) or longitudinal spin density wave AF(2)); and (iii) commensurate AF(0). It has been of great interest to determine the boundaries of the magnetic-phase diagram and the nature of the corresponding transitions as a function of temperature and pressure. Numerous experimental techniques have been used for these purposes. Among these are neutron diffraction,[1,2] electrical resistivity,[3-8] magnetic susceptibility,[9-11] thermal expansion,[1,11-14] specific heat,[15] infrared reflectivity,[16,17] sound velocity, and elastic constants.[14] The present study was undertaken to investigate the thermodynamic characteristics of magnetic transitions in some Cr-Fe samples explored earlier[4] by electrical-resistivity measurements. When this investigation was started, no specific-heat data of any kind existed for the Cr-Fe system. During the course of this work, the specific-heat studies by Suzuki[15] were published. Our results on heat capacity and their significance for some Cr-Fe alloys, obtained using a different experimental technique than that used by Suzuki, are briefly described below.

II. EXPERIMENTAL CONSIDERATIONS

Heat capacities were measured in the neighborhood of the corresponding magnetic transitions on polycrystalline Cr and polycrystalline Cr-Fe alloys containing 2.3-, 3.3-, and 4.9-at.% Fe. The samples of these materials were prepared from the original arc-melted ingots used in the electrical resistivity work described elsewhere.[4,18] The selection of the particular alloy concentrations was stimulated by existence of large electrical resistivity anomalies observed in these alloys at the magnetic transitions. Heat capacity data were obtained using a Perkin-Elmer differential calorimeter, DSC-2.

The instrument has been described by Watson *et al.*[19] The theory of this dynamic thermal measurement has been given by Gray[20] and O'Neill.[21] A comprehensive review also was published recently by Flynn.[22]

The almost identical sample and reference holder cups of the differential scanning calorimeter contain heaters and platinum resistance thermometers. The temperature of the holders is controlled to follow the predetermined temperature program. The power difference which is required to keep both sample and reference holders at nearly the same temperature is characteristic of the enthalpy rate difference between sample and reference material.

The quantities directly measured by the DSC are the power difference $\dot{Q}$ and the program temperature T_P. The latter is a linear function of time

$$T_P = T_0 + \dot{T}_P t , \tag{1}$$

where $\dot{T}_P$ is the constant rate of heating. The net enthalpy rate difference is calculated by subtracting the empty calorimeter baseline $\dot{Q}_0$:

$$\dot{q} = \dot{Q} - \dot{Q}_0 . \tag{2}$$

The enthalpy scale of the instrument must be calibrated with substances of known thermal properties. We used 99.9999%-purity Al both for the reference material and calibrant, since its thermal diffusivity and the temperature dependence of its specific heat are on the same order of magnitude as those of our Cr alloys. The thermal properties of Al have been compared with those of NBS-calibrated Al_2O_3 in separate measurements and found to agree with the accepted values to within 2%.

In the steady-state condition the enthalpy rate difference $\dot{q}_{st}$ is determined by the total heat capacity of the sample C_S and reference material C_R.

$$\dot{q}_{st} = \dot{T}_P(C_S - C_R) . \tag{3}$$

In the temperature region of a phase transformation there is an excess contribution to the enthalpy change $\dot{q}_{ex}$,

$$\dot{q} = \dot{T}_P(C_S - C_R) + \dot{q}_{ex} . \tag{4}$$

The separation of the measured enthalpy flow rate to a background and an excess heat flux $\dot{q}_{ex}$ facilitates the comparison of different processes. The heating-rate dependence of the excess heat-flux amplitude for a clear first-order phase transition will be discussed in Sec. III. As a higher-order phase transition can be characterized with an extra heat-capacity contribution, the measured enthalpy rate difference is proportional to the heating rate.

The enthalpy flow rate can always be converted to apparent heat capacity by extending Eq. (3) to the transformation region. The apparent heat capacity is equivalent with the thermodynamic heat capacity outside the transformation region and characterizes the thermal properties of the sample at the transition. The apparent nature is clearly seen, as the heat capacity defined this way should be dependent on the heating rate, e.g., at a first-order phase transformation. The area between the apparent heat capacity and the background is ΔH, the total enthalpy change (latent heat) of the transformation.

The background, i.e., the slight variation of heat capacity with temperature, could be determined from the measured instantaneous enthalpy rate difference in the absence of a transition. A more accurate method, not vulnerable to thermal lag errors, is suggested by Flynn.[23] The enthalpy change of the sample δH is measured in a temperature interval δT, and an average heat capacity is calculated as $C = \delta H/\delta T$. A common background heat capacity for the total set of alloys has been determined this way.

As the directly measured quantity is the program temperature, the sample temperature must be calibrated and corrected for thermal lags. The temperature scale is calibrated at the lowest heating rate (0.31 K/min) with the known transformation temperature of cyclohexane (186.1 K) and In (429.8 K). The calibration has been checked at the melting point of ice (273.2 K) and found to be correct within 0.5 K.

Energy is supplied to the sample and reference material through the characteristic heat resistance of the instrument. In a good approximation sample and reference holder can be characterized with the same heat resistance R. The heat-flow rate is expressed by the Newton law of heat transfer

$$\dot{q} = \dot{q}_{sample} - \dot{q}_{ref} = \frac{T_P - T_S}{R} - \frac{T_P - T_R}{R} , \tag{5}$$

where T_P, T_S, and T_R denote the program, the sample, and the reference temperature. Equation (5) can be reduced to

$$\dot{q} = (T_R - T_S)/R , \tag{6}$$

which is used for thermal-lag correction.

The thermal lag of the thermally inert reference material is determined by its thermal response time $\tau_R = RC_R$

$$T_R = T_P - \tau_R \dot{T}_P . \tag{7}$$

The sample temperature is calculated from (4), (6), and (7) as

$$T_S = T_P - \tau_S \dot{T}_P - R\dot{q}_{ex} , \tag{8}$$

where the thermal response time for the sample $\tau_S = RC_S$. The thermal lag of the sample in the absence of any transformation $\Delta T_S = \tau_S \dot{T}_P$ has been measured with the method suggested by Richardson and Savill.[24] The enthalpy change of the sample after termination of the linear heating program δH_a measures the steady-state thermal lag as $\Delta T_S = \delta H_a / C_S$.

The temperature deviation $\delta T_S = R\dot{q}_{ex}$ caused by the phase transformation of the Cr alloys can be estimated using the measured $\dot{q}_{ex}$ and the calculated[20] R values. Since δT_S was found to be less than the instrument nonlinearity error (0.5 K), it has been neglected, except for the avalanche transition (see below). In this special case Eq. (8) is used for estimating the temperature jump of the sample.

III. RESULTS AND DISCUSSION

It has been established that the symmetry of the Cr lattice changes from cubic to orthorhombic at the Neél temperature T_N [AF(1)$\rightleftarrows P$ transition] and from orthorhombic to tetragonal at the spin-flip temperature T_{sf} [AF(1)$\rightleftarrows$AF(2) transition]. By definition, a first-order transition is characterized by discontinuous first derivatives of the Gibbs function (such as volume, specific heat, etc.) at the transition and exhibits some latent heat. The second- (or higher) order transitions have discontinuities in second (or higher) derivatives and no latent heat. Using the criterion that one of the most reliable methods for the determination of the first-order transition is the presence of latent heat, Polovov[25] has clearly demonstrated that the transitions at T_N and T_{sf} in pure, strain-free single crystals of Cr are first order. The latent heat associated with the $AF(1) \rightarrow P$ transition is very small, i.e., 1.13 ± 0.13 J mole^{-1}, in good agreement with the more recent determination, 1.10 ± 0.10 J mole^{-1}, by Benediktsson *et al.*[26] The latter investigators also confirmed the existence of latent heat in well-annealed polycrystalline samples. However, the order of the two transitions mentioned above are very sensitive to impurities and strains. Thus, for example, the sharp peak in the specific-heat curve for a single crystal is drastically reduced and broadened for a strained polycrystalline material.[25] The weakness of the first-order transition in pure Cr has stimulated theoretical development[27,28] proposing that the experimental evidence of a first-order transition can also be interpreted in terms of divergent fluctuations at a second-order transition.

Figure 1 shows the specific heat C of our polycrystalline Cr as a function of the absolute temperature T in the neighborhood of $T_N = 311$ K. Our values of C are in good agreement with corresponding values obtained by Polovov.[25] Excess heat capacity is observed in a wide temperature range, as is characteristic of a second-order phase transition. However, due to possible interference with first-order effects we were unable to separate unambiguously the different contributions in the apparent heat capacity.

In principle, an unbroadened first-order phase transition without any kinetic restraint is detectable from the heating-rate dependence of the excess heat-flux amplitude. The $q_{ex} - T_p$ relation according to Gray[20] is

$$\dot{q}_{ex}^{max} = \dot{T}_p C_S[(1 + \Delta H / R C_S^2 \dot{T}_p)^{1/2} - 1] . \qquad (9)$$

In order to test the detectability of very small heat effects coupled with a significant total heat capacity, we observed the melting of 0.2-mg In on top of our 200-mg pure Cr sample (ΔH_{melt} for 0.2-mg In $\simeq \Delta H_{1st\ order}$ for 200-mg Cr $\simeq 4$ mJ). The measured heat flux, shown in Fig. 2, agrees quite well with that calculated from Eq. (9). No trace of a similar behavior can be observed at T_N of Cr. As the apparent specific heat is independent of the heating rate (see Fig. 1), the excess heat flux is a linear function of it. The contribution of the transformation should be 10 times greater than that of the excess heat capacity at 0.31 K/min heating. This absence of measurable heat effects shows that the first-order transformation in Cr is either broadened by a

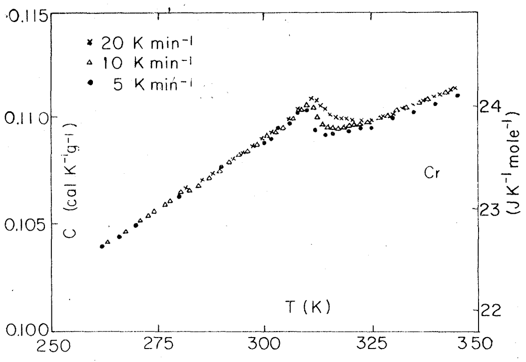

FIG. 1. Specific heat of Cr measured with different heating rates.

distribution of T_N in the sample or is sluggish due to kinetic restrictions. With the more sensitive method of Benediktsson *et al.*[26] it would be possible to choose between these possibilities. In the case of a T_N distribution, the measured heat flux should be independent of the heating rate so long as the temperature inhomogeneity in the sample is much smaller than the width of the T_N distribution. If the transformation rate is limited by a kinetic restriction, the peak temperature could be shifted to higher temperatures with increasing heating rates.

Figures 3 and 4 show C as a function of T, using a 5-K/min heating rate, for Cr and alloys containing 2.3-, 3.3-, and 4.9-at.% Fe. The crosses below the C vs. T curve show the background determined using the enthalpimetric mode. It can be seen that the peaks become considerably larger in comparison with pure Cr. The high and narrow peak of the Cr–3.3-at.%-Fe alloy is particularly noteworthy. The strong dependence of apparent specific heat upon heating rate is illustrated in Fig. 5. At first glance it would appear that this behavior is indicative of a sharp first-order phase

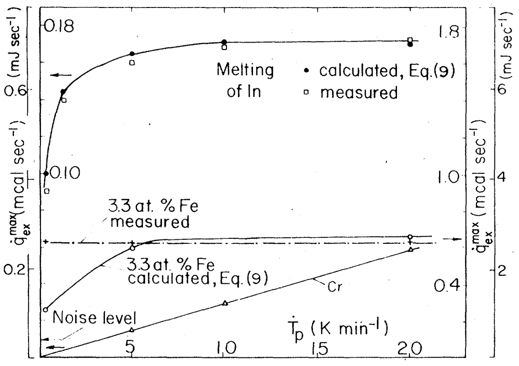

FIG. 2. Dependence of heat-flux amplitude upon heating rate.

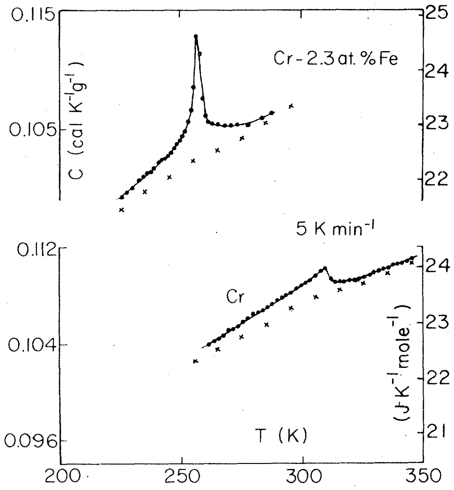

FIG. 3. Specific heat of Cr and Cr–2.3-at.% Fe.

transition. Actually this is not the case.

In an ideal first-order transition (such as melting of a high-purity substance) the sample temperature T_S does not change during the transition $T_S = T_{tr}$. As the temperature of the inert reference material follows the linear heating program, there is an excess heat flux in the transformation region. It can be calculated from Eq. (6) as

$$\dot{q} = [T_R(t=0) + \dot{T}_P t - T_{tr}]/R = \dot{q}_{st} + (\dot{T}_P/R)t \qquad (10)$$

between $t=0$ and $t=t_{end}$, while $T_S = T_{tr}$.

This behavior can be seen from the In melting thermogram of Fig. 6. If the first-order transition is broadened by some disturbance, T_S may not be constant but will increase slower than T_R. The $\dot{q}_{ex}$ vs t curve will not be linear, but the average slope must be smaller than that of an ideal first-order transition.

For Cr–3.3-at.% Fe Fig. 2 shows a complete independence of heat-flux amplitude from the heating rate. A relative insensitivity is expected only at higher heating rates according to Eq. (9), which describes well the sharp first-order transformations. The discrepancy observed at slow heating shows the inapplicability of Eq. (9) and challenges the first-order interpretation of the observed transformation. Moreover, the slope of the heat-flux-versus time curve is significantly greater than that for a first-order transition, as shown by Fig. 6. From Eq. (8) we conclude that T_S decreases during the transformation. From the calculated enthalpy change $\Delta H = 11 \pm 1$ J/mole and the measured heat capacity, the temperature jump can be estimated as $\Delta T \simeq -0.5$ K. This value is in good agreement with the lower limit for the temperature drop calculated from the measured heat-flux amplitude. Using Eq. (8) with $R = 0.12$ K sec/mJ calculated according to Gray[20] gives

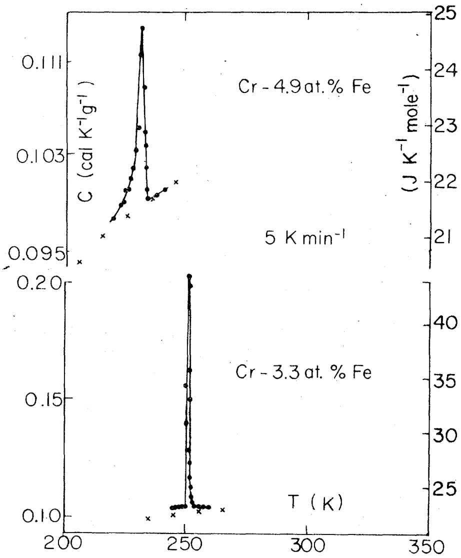

FIG. 4. Specific heat of Cr–3.3-at.% Fe and Cr–4.9-at.% Fe.

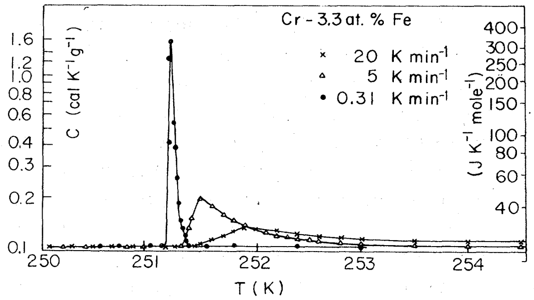

FIG. 5. Specific heat of Cr–3.3-at.% Fe measured with different heating rates.

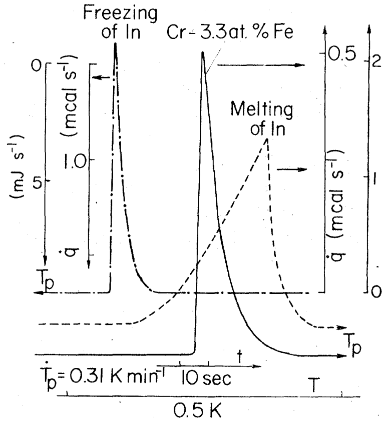

FIG. 6. Comparison of melting, crystallization, and avalanche transition thermograms.

$\Delta T_{\text{peak}} = -0.35$ K. $|\Delta T_{\text{peak}}|$ is bound to be smaller than $|\Delta T|$ because of the finite instrumental response time, $\tau_X \simeq 1.5$ sec,[23] which is comparable with the duration of the transformation.

Apparently, the antiferromagnetically ordered Cr–3.3-at.%-Fe sample enters a superheated metastable magnetic phase before becoming paramagnetic. The thermal behavior is reminiscent of a supercooled liquid at crystallization (see Fig. 6), and suggests a nucleation controlled-phase transformation. For this reason we call this transformation an avalanche transition. Neither the nucleation process nor the magnetic structure of the metastable phase are understood at the present time. It should be noted that the specific-heat plots obtained by Suzuki[15] for 3.0- and 4.0-at.% Fe in Cr alloys also exhibit very high peaks. It is possible that these reflect the avalanche process described above. It definitely appears that the region between 3- and 4-at.% Fe of the first-order (according to Suzuki) phase boundary between 2.5- and 4.9-at.% Fe separating the *P* and AF(0) phases possesses some strange features. In fact, we suspect that the avalanche effect might exist in this narrow compositional region. Work on other Cr-Fe alloys with Fe content between 3 and 4 at.% is needed to clarify this situation. It should be remarked that the avalanche effect is absent in our Cr–4.9-at.%-Fe sample. Furthermore, recent studies of the Young and the bulk modulus by Hausch and Török[14] show very dramatic changes in these quantities in Cr–3.8-at.%-Fe alloy at the magnetic transition. This observation may have bearing on our heat capacity observations in the Cr–3.3-at.%-Fe sample.

Finally, we note that the peaks of the specific-heat curves for Cr alloys containing 2.3-, 3.3-, and 4.9-at.% Fe occur at about 256, 251, and 231 K, respectively. These temperatures are in excellent agreement with previous determinations of T_N by electrical-resistivity techniques.[4]

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