Specific Heat of Cr-Fe Alloys from −140° to 350°C*

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(Received August 14, 1961)

The specific heat of bcc iron-chromium alloys has been measured in an adiabatic calorimeter in the temperature range from −140 to 350°C. Isothermal plots of c_p vs composition revealed two maxima at higher temperatures. One occurred independently of temperature at 19 at. % Fe and was associated with the peak in the density-of-states curve; the other was temperature dependent and was associated with the transition from ferromagnetism to paramagnetism. Lattice and electronic contributions could be separated from each other for alloys with high chromium concentration. The Debye θ did not vary noticeably with composition, but the electronic specific heat showed a maximum.

INTRODUCTION

CHENG, Wei, and Beck[1] measured recently the low temperature specific heat c_p of transition element alloys. They separated c_p for Cr-Fe alloys into lattice and electronic components and found that the electronic term had a maximum at 19 at.% Fe. The lattice term, characterized by the Debye temperature θ_D, showed an irregular behavior, with very low θ_D for chromium-rich alloys, a maximum θ_D near 19 at. %, and decreasing θ_D values for further increasing Fe concentrations. Room temperature specific heat measurements[2] confirmed the suggestion, that the peak in the γ vs. composition curve was electronic in origin. These measurements were in the present work extended over a range of temperatures in order to clarify the question, whether the Debye temperature showed anomalies also at higher temperatures, and how large the electronic specific heat is and at what composition it had a maximum.

EXPERIMENTAL PROCEDURE

Specimens were prepared by melting electrolytic chromium and iron in an induction furnace under He atmosphere, then annealed for three days at 1200°C in a 92% helium+8% hydrogen atmosphere and quenched in water. The iron-rich alloy specimens were the same as were previously used for the room temperature measurements. Chromium-rich specimens were newly prepared for the present work. The gas analysis of these alloys gave oxygen as the main impurity. The highest amount of oxygen was found in the alloy with 17.5 at. % Fe (0.47%). The lowest in the alloy with 19.9 at. % Fe and 21.8 at. % Fe (0.24%).

The specific heat was measured in an adiabatic vacuum calorimeter of standard design.[3] It consisted (Fig. 1) of an outer stainless steel tube (a), radiation shield (b), heater (c), and a second radiation shield (d) which surrounded the specimen assembly (e). This assembly consisted of the cylindrical specimen (f) of

about 30 g weight, a constantan wire (g) as heating element, inserted into holes of the specimen, and a copper foil cover (h) of about 0.1 mm thickness, to prevent heat loss from direct radiation from the heater. The power for heating the specimen was kept nearly constant during any one experiment giving a heating rate of approximately 3°C/min. The temperature difference Δt between specimen and radiation shield was measured with an iron-constantan-iron differential thermocouple.[1] Δt was kept usually below 0.1°C by manually adjusting the power supply of the radiation shield heater. The specimen temperature was measured with an iron-constantan thermocouple (m). The specific heat $C(T)$ of the heater assembly was determined using the equation $C(T) = (IV/4.185)(\Delta P/\Delta t)/(\Delta R/\Delta z) = Q(t)/\Delta t$. Current I and voltage drop V of the heater was measured with standard resistance and a potentiometer to 0.1%. The time interval Δz to increase the thermopower of the iron-constantan thermocouple by ΔP was measured to 0.5%. ΔP was also determined to an accuracy of 0.5%. $\Delta P/\Delta t$ was taken from the National Bureau of Standards circular 561; above −100°C the accuracy of these values is estimated to
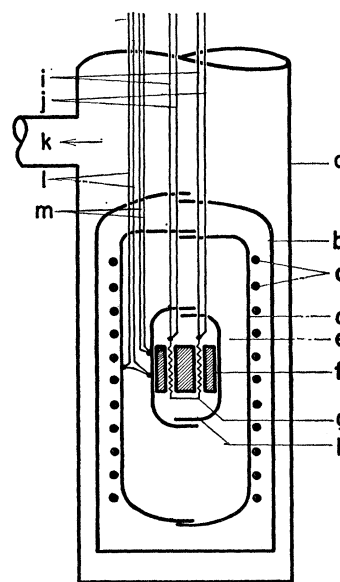

Fig. 1. Schematic plan of vacuum calorimeter. (a) Stainless steel tube, (b) radiation shield, (c) heater for radiation shield (d), (d) radiation shield, (e) specimen assembly, (f) specimen, (g) specimen heater, (h) copper foil (0.1 mm thick), (i) specimen heater current lead, (j) potential leads, (k) to pump, (l) differential thermocouple, (m) thermocouple.

[1] C. H. Cheng, C. T. Wei, and Paul A. Beck, Phys. Rev. **120**, 426 (1960).
[2] K. Schröder, Phys. Rev. **117**, 1500 (1960).
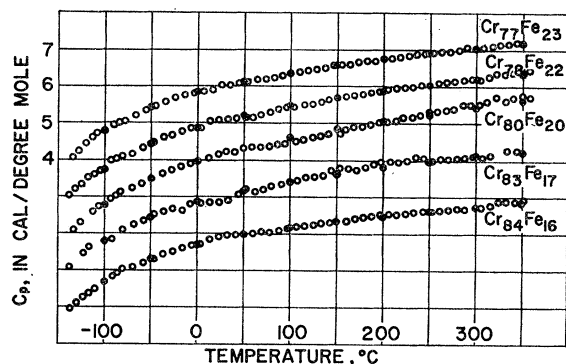[3] A. Eucken, *Handbuch der Experimentalphysik* (Akademische Verlagagesellschaft, Leipzig, 1929), Vol. 8, p. 110.

Fig. 2. Specific heat of bcc Cr-Fe alloys with 16 to 23.4 at. % Fe. Open circles: experimental values. Full circles: best-fit function $c_p = c_D(\theta,t) + \gamma'T$. Ordinate scale given for top curve. For each successive curve the scale is displaced downward by one unit.

0.2%. The specific heat of the specimen c_p was found by subtracting from C the calculated heat of heater wire, copper foil, etc., c_p is estimated to be correct to 1.5% in the temperature range from $-100°$ to $300°C$, decreasing in accuracy for temperatures below $-100°C$ because of uncertainties in $\Delta P/\Delta t$, and above $300°C$ because of increased heat transfer by radiation between specimen assembly and radiation shield.

RESULTS AND DISCUSSION

The experimentally found values of the specific heat c_p are given in Figs. 2 to 4. The reproducibility of these curves was within the experimental accuracy, except for ferromagnetic alloys near and above the Curie temperature. The c_p values of alloys with more than 35 at. % Fe agree within the experimental reproducibility with the earlier room temperature measurements.[2] Since the same specimens were used, this indicated that the experimental techniques were reliable. Larger deviations for the alloy with 35 at. % Fe should be attributed to the fact, that the Curie temperature of this alloy is very close to room temperature. Also, if there is a marked temperature dependence of c_p, which is possible near the Curie temperature, the kerosin bath calorimeter should give a more precise c_p value, because the temperature increase Δt was only 3°C, compared with 10°C in the vacuum calorimeter. Furthermore, there is always a temperature gradient in the specimen during continuous heating in the vacuum calorimeter, so that only a mean specific heat is measured. But in the kerosin bath calorimeter, the specimen has at the beginning and at the end of the measurements a practically uniform temperature.

A new set of specimens had to be prepared for alloys with less than 30 at. % Fe. The differences between the present results with these specimens and the previous room temperature results with the first set of specimens are slightly larger than the experimental error. But it will be seen later, that the interpretation of the results is unchanged.

Table I. Alloy compositions for the two maxima in the specific heat and for the Curie point at various temperatures.

t (°C)	M_1 (at. % Fe)	M_2 (at. % Fe)	T_C (at. % Fe)
-100	19		
0	20	40	32
100	19	45	36
200	19	50	43
300	19.5	53	47
350	19.5	55	52

Figure 5 gives the isothermal specific heat data c_p vs composition. c_p values for pure chromium were taken from the literature.[4-7] The higher temperature curves have two maxima M_1 and M_2. These maximum specific heat values decrease with decreasing temperature. The maximum M_1 occurs always near a fixed composition of about 19 at. % Fe, while the other maximum M_2 shifts with decreasing Fe concentration to lower temperatures. Low temperature specific heat measurements[1] showed that the electronic specific heat has a maximum at 19 at. % Fe. Hence, M_1 should be associated with the density of state curve. Table I shows that the temperature-composition relation for M_2 is very similar to that of the Curie temperature T_C.[8] But for a given temperature M_2 occurs always at a slightly higher iron concentration than expected from magnetic measurements. This means that the temperature of M_2 for a fixed composition is below the Curie temperature. This is also observed for pure iron,[9] and, therefore, one should associate M_2 with the transition from the ferromagnetic to the paramagnetic state, in spite of the fact, that most specific heat curves are smooth and show no sharp peak near the Curie tem-
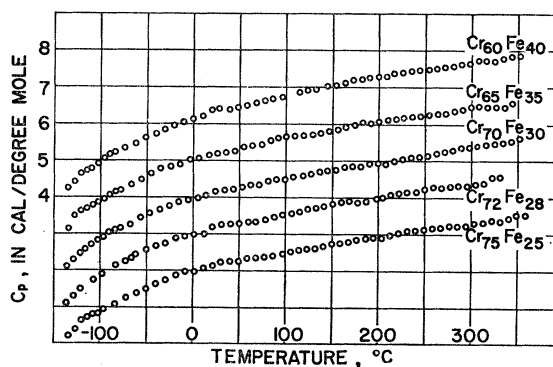

Fig. 3. Specific heat of bcc Cr-Fe alloys with 25 to 40 at. % Fe. Ordinate scale given for top curve. For each successive curve the scale is displaced downward by one unit.

[4] C. T. Anderson, J. Am. Chem. Soc. 59, 488 (1937).

[5] P. Nordmeyer and A. L. Bernulli, Ber. deut. physik. Ges. 6, 175 (1907).

[6] P. Schübel, Z. anorg. Chem. 87, 81 (1914).

[7] S. Umino, Sci. Repts. Tohoku Univ. 15, 597 (1926).

[8] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, New York, 1958), p. 525.

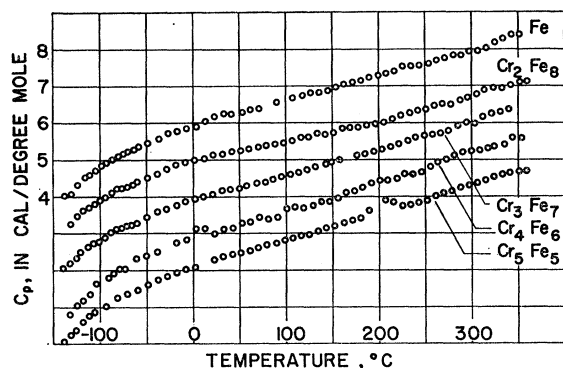[9] E. Lapp, Ann. phys. 6, 826 (1936).

Fig. 4. Specific heat bcc of Cr-Fe alloys with 50 to 100 at. % Fe. Ordinate scale given for top curve. For each successive curve the scale is displaced downward by one unit.

perature. Naturally, in an alloy one would not expect a sharp λ-point as observed in pure elements because of the statistical composition variations on a microscopic scale. For instance, Grew[10] found that the point of the specific heat curve of an alloy with only 21.2% Cu in Ni had nearly disappeared. But statistical composition fluctuations are not likely to be responsible for the complete disappearance of the peak in the specific heat curve for chromium rich iron alloys. These conditions are not completely clarified at present.

For alloys with 23 at. % Fe, or less, T_C is well below $-140°C$. For these chromium rich alloys c_p should, therefore, consist of the lattice term c_L, the electronic term c_E, and the term due to thermal expansion c_p-c_v. Both c_E and c_p-c_v are linear in temperature, so that one obtains $c_p=c_L+\gamma T+(V\alpha^2/\chi)T$ assuming that the electronic specific heat is still linear with temperature in this temperature range. It is usually assumed that c_L can be approximated by the Debye function c_D in the temperature range from $-140°$ to $350°C$ and therefore $c_p=c_D(T,\theta_D)+\gamma'T$, with $\gamma'=\gamma+\alpha^2V/\chi$. A series of c_p values with θ_D and γ' as parameters were calculated for temperatures of -100, -50, 0, $\cdots$, $350°C$. Table II gives those θ_D, γ' values, for which the sum of the terms $[c_p(\text{calc})-c_p(\text{meas})]^2$ for $t=-100$, -50, 0, $\cdots$, and $350°C$ is a minimum. θ_D is thereby determined to $\pm5°K$ and γ' to $\pm0.5\times10^{-4}$cal/mole deg^2. The best fit functions with these θ_D and γ' values

TABLE II. Electronic specific heat coefficients and degeneracy temperatures for Cr-Fe alloys.

Alloy (at. % Fe)	θ_D (°K)	γ (cal/deg^2 mole)	γ (cal/deg^2 mole)	γ (low temp) (cal/deg^2 mole)	T_0 (°K)
15.9	440	16.3×10^{-4}	16.2×10^{-4}	32×10^{-4}	980
17.5	440	23.0×10^{-4}	22.9×10^{-4}	38×10^{-4}	1100
20.1	465	29.4×10^{-4}	29.3×10^{-4}	37×10^{-4}	1500
21.8	455	24.9×10^{-4}	24.7×10^{-4}	33×10^{-4}	1380
23.4	440	22.0×10^{-4}	21.9×10^{-4}	32×10^{-4}	1220

[10] K. Grew, Proc. Roy. Soc. (London) **A145**, 509 (1934).

are indicated in Fig. 2. They agree reasonably well with the measured values. No values of the compressibility of Fe-Cr alloys as a function of composition are known to the author. Therefore it was assumed that $(V\alpha^2/\chi)T$ varied linearly with the composition. Because the term c_p-c_v is small compared with c_E and d_L, even a large error in this term should have no marked effect on the calculation of γ. Comparison with the low-temperature γ values, which are also given in Table II, shows that the high-temperature γ values are significantly lower. Stoner[11] gave electronic specific heat as a function of powers of (T/T_0), with T_0 as the degeneracy temperature. Using terms up to $(T/T_0)^3$, and assuming that the high-temperature γ values are representative for the temperature $T=400°C$, one gets within the experimental error $T_0\sim1200°K$ (Table II). The experimental accuracy is not sufficient to decide if the degeneracy temperature is really so low, or if the low-temperature values are not only electronic, but comprise also other terms in the low-temperature specific heat linear in T. It should be pointed out that in this composition range the low-temperature measurements were carried out below the Curie point, while the present measurements above it. It is significant that in both sets of measurements the maximum value of γ occurred near the same composition, namely 19 at. % Fe. Mott and Jones[12,13] find for nickel $T_0=2470°K$ and palladium $T_0=1750°K$. The value of $1200°K$ agrees with these figures within a factor of 2. But one would expect with such low T_0 values that c_p calculated as $c_p=c_D(\theta_D,T)+\gamma'T$ should be systematically slightly higher than the measured c_p value at 350° (Fig. 2). This is not the case.

The Debye temperature of alloys with 17 to 23 at. % Fe does not change much with the composition (Table II). These θ_D values are similar to those usually attributed to the transition elements. Cheng, Wei, and
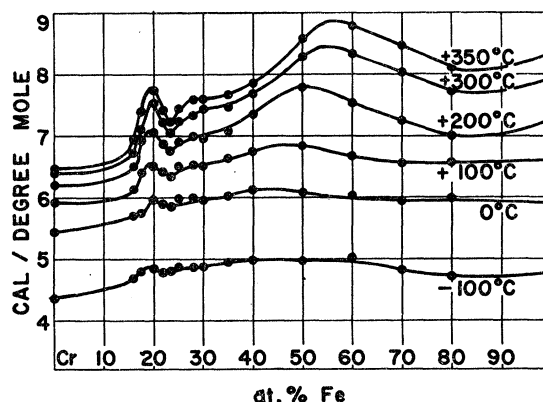

Fig. 5. Specific heat versus composition at various temperatures.

[11] E. C. Stoner, Phil. Mag. **21**, 145 (1936).
[12] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 193.
[13] J. de Launay, Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, p. 233.

Beck[1] found in their low-temperature specific heat measurements with Cr-Fe alloys a strong variation of the Debye temperature with the composition. Near the peak of the density-of-states curve, θ_D was very large, but alloys with 10 at. % and 15 at. % Fe had an unusually low θ_D. It seems, therefore, likely that the low-temperature specific heat term proportional to T^3 is not due to lattice vibrations only, but that it comprises other contributions to the specific heat as well.

CONCLUSIONS

The specific heat of chromium-rich Cr-Fe alloys measured in the temperature range from $-140°$ to $350°C$ can be separated into electronic and lattice specific heats. The lattice specific heat is described by the Debye function, with θ_D between $440°$ to $465°K$. Because these values agree reasonably well with accepted θ_D values for iron and chromium, it is suggested that the different θ_D found at low temperatures are not real, but due to additional T^3 terms in the specific heat. The electronic specific heat in our experiments is within the experimental accuracy described by $c_E = \gamma T$. γ shows a maximum at the composition of 19 at. % Fe, the same composition at which a maximum was observed at low temperatures. This indicates that the term linear in T in the specific heat is essentially an electronic contribution and it reflects a high density of states.

Interband Transitions in Superconductors

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(Received October 9, 1961)

When the photon energy is such that an interband transition occurs between the valence and conduction bands in the normal state, small differences in the optical properties of the normal and superconducting metals can arise. Using a simple energy-gap model for the superconductor, the change in the reflectivity and transmission is calculated and is shown to be measurable over a narrow frequency range, assuming realistic values for the pertinent parameters. This type of experiment may be useful for studies of both interband transitions in normal metals and anisotropy of the energy gap in superconductors.

I. INTRODUCTION

THE optical properties of superconductors have been studied extensively in the far infrared region[1] ($h\nu \approx 3.5kT_c$) and in the infrared region[2,3] ($h\nu \gg 3.5kT_c$). Ramanathan[3] found the change in the absorptivity of normal and superconducting Sn at 14 μ to be less than the 0.3% limit of his sensitivity. (At 14 μ, Sn has $h\nu/kT_c \approx 280$.) The far infrared measurements of Richards and Tinkham[1] show the absorptivity to be essentially the same in the normal and superconducting states for $h\nu/kT_c > 6$. It has also been noted by Tinkham and Ferrell[4] that the sum rule on the real part of the conductivity also implies that for $h\nu \gg 3.5kT_c$,

the conductivity is the same in the normal and superconducting states.

This note points out that when the photon energy is such that an interband transition occurs between the valence and conduction bands in the normal state, small differences in the optical properties of the normal and superconducting metals can arise. Using a simple energy-gap model for the superconductor, the change in the reflectivity and transmission is calculated and is shown to be measurable, assuming realistic values for the pertinent parameters. This type of experiment may be useful for studies of both the interband transitions in normal metals and the anisotropy of the energy gap in superconductors.

II. CALCULATION

For simplicity, a parabolic two-band model is chosen with the energy extrema of the valence and conduction bands taken at $k=0$. In the superconducting state, an energy gap of 2Δ is introduced symmetrically about the Fermi energy in the conduction band, as is shown in Fig. 1. The valence bands for the normal metal and

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[2] J. G. Daunt, T. C. Keeley, and K. Mendelssohn, Phil. Mag. **23**, 264 (1937).
[3] K. G. Ramanathan, Proc. Phys. Soc. (London) **A65**, 532 (1952).
[4] M. Tinkham and R. A. Ferrell, Phys. Rev. Letters **2**, 331 (1959).