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Specific Heat of Chromium-Iron Alloys at Room Temperature*

K. Schröder
University of Illinois, Urbana, Illinois

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The specific heat of bcc iron-chromium solid solution alloys was measured at room temperature and then calculated under simplified assumptions from lattice, magnetic, and electronic terms. The magnetic atomic heat was evaluated using the simple Weiss theory. The electronic term was assumed to be equal to γT, where the value of γ used was that obtained earlier from low-temperature specific heat measurements. The lattice term was taken to be the same for all alloys. Reasonable quantitative agreement between the calculated and the measured values was achieved.

INTRODUCTION

THE specific heat, c, of bcc iron-chromium solid solutions was recently measured by Wei, Cheng, and Beck[1] at low temperatures. They found that for most alloys c could be separated into a linear and a cubic term in T. The temperature coefficient of the term linear in T was found to have unusually large values for alloys near 19 at. percent Fe. Since the Curie temperature is known to decrease to quite low values in this composition range, it appeared that the high values of the temperature coefficient may be partly due to the magnetic transformation. It is possible to check whether or not this is so by measuring c at room temperature, which is for these alloys far above the Curie point. If the term linear in T represented the electronic specific heat, then the high value of γ should not change appreciably up to temperatures higher than room temperature. On the other hand, if this term be due to the magnetic transformation, the value of γ above the Curie temperature (e.g., at room temperature) should decrease considerably.

EXPERIMENTAL PROCEDURE

Specimens of about 100 grams weight were prepared by melting electrolytic chromium and iron in an induction furnace under He atmosphere. The alloy specimens were annealed for 3 days at 1200°C in an 92 percent He+8%H_2 atmosphere and they were quenched into cold water. Spectroscopic analysis indicated that the only impurity was manganese (approximately 0.1%).

The specific heat c_p was measured at room temperature, using a standard method.[2] The heat capacity of the Dewar with kerosene, stirrer, and heater was measured by heating it up with a known amount of electric energy E. Current and voltage drop in the heater was measured, using a potentiometer and precision resistors. The current was switched off automatically after 72 seconds. The temperature increase T was measured with a thermopile, consisting of 10 copper-constantan thermocouples. The thermopile was calibrated with a Beckmann thermometer. The measurement was then repeated with a specimen submerged in the kerosene bath. The heat capacity E/T of the Dewar with kerosene and specimen minus the heat capacity of the Dewar with kerosene, but without specimen, is equal to the heat capacity of the specimen. The electrical energy E could be measured to an accuracy of $\pm 0.2\%$. The estimated accuracy of the temperature increase due to the heating was $\pm 0.3\%$, and that of the calculated specific heat of the specimen $\pm 2\%$.

RESULTS AND DISCUSSION

The experimental values of c_p are given in Fig. 1. It was found that c_p depended on the duration of the homogenizing anneal. In the present work all specimens were annealed for 3 days (the same thermal treatment as that given to the specimens used by Wei, Cheng, and Beck[1]). Figure 1 shows that c_p has two peaks, one at 19 at. percent Fe, and the other at 35 at. percent Fe. The former lies at the position where the specific heat coefficient γ has its maximum,[1] the latter in the vicinity of the composition, 33 at. percent Fe, where the Curie

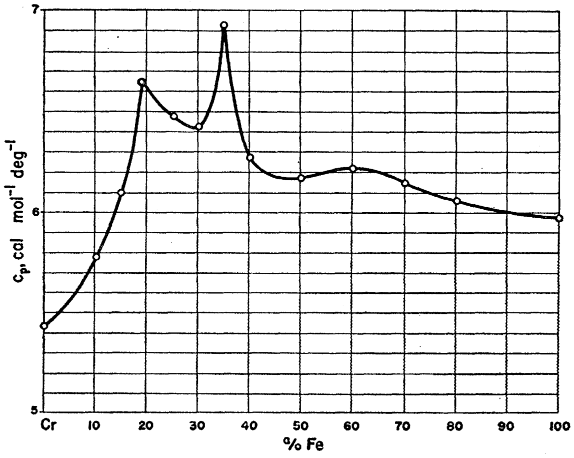

FIG. 1. Measured specific heat, c_p, at room temperature vs composition for bcc alloys of Cr and Fe.

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[1] Wei, Cheng, and Beck, Phys. Rev. Letters 2, 95 (1959).

[2] A. Eucken, *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig, 1929), Vol. 8, Part 1.

temperature is room temperature, according to Pomey.[3] These results clearly show the separation of the maximum in the specific heat at 19 at. percent Fe from that due to the magnetic transformation. The fact that at room temperature a maximum occurs at the same composition (19 at. percent Fe) where the sharp peak of the specific heat coefficient γ was found at liquid helium temperatures further suggests that this peak is not connected with the magnetic transformation.

For a quantitative discussion one has to separate the terms of c_p. It may be assumed that c_p is equal to the sum of c_L, c_E, c_M, and c_p-c_v, where c_L is the lattice specific heat, c_E the electronic specific heat, and c_M the magnetic specific heat. c_p-c_v cannot be calculated for the alloys, because neither the compressibility nor the thermal expansion coefficient is known. It was assumed that c_p-c_v varies linearly with composition from chromium to iron.

The lattice specific heat c_L for chromium can be calculated as $c_L=c_p-(c_p-c_v)-c_E$, with $c_p=5.43$ cal mole^{-1} deg^{-1}, $c_p-c_v=T\alpha^2V/\chi_0\simeq 7.5\times10^{-2}$ cal mole^{-1} deg^{-1} and $c_E=\gamma T=0.12$ cal mole^{-1} deg^{-1}. The influence of the antiferromagnetism is neglected, because there is no discontinuity in c_p at the Néel temperature of Cr, which is close to room temperature. c_L (Cr) is therefore 5.28 cal/mole. This corresponds to a Debye temperature of $\theta=470$°K. A similar estimate for iron is not possible, because the magnetic specific heat c_M is not known accurately. It was assumed that in first approximation c_L is the same for all alloys and for iron and that it is equal to c_L (Cr). This assumption is justified because the vibrational spectrum should not change very much with alloying if the structure remains bcc and both atoms have nearly the same weight. Also, it is well known that even large changes in the vibrational spectrum influence the Debye function only slightly.[4]

Figure 2 gives the curves of $c_E=\gamma T$, c_E+c_M and $\Delta c=c_p-c_L\,(\mathrm{Cr})-(c_p-c_v)$. c_E was calculated from the γ values measured by Wei, Cheng, and Beck.[1] Accurate calculation of c_M is not possible, because neither the molecular field constant N nor the saturation magnetization of the specimens as a function of composition and temperature is known. But it was attempted to calculate c_M with the simple Weiss theory[5] using the Curie temperatures published by Pomey[3] and values of the saturation moment n_0 calculated by Fallot.[6] The sum of c_E and c_M agrees with Δc within 4% for most alloys. Exceptions are alloys with an iron concentration of 25 to 40 at. percent. This agreement for the iron-rich alloys seems to be good, if one keeps in mind that c_p measurements of ferromagnetic materials are not very reliable, probably, because they depend to a large extent on impurities and thermal treatment.[5] The larger deviations of the experimental values of c from the calculated ones near 35 at. percent Fe are due to the fact that the simple Weiss theory is not a good approximation near the Curie temperature. It is not known how c_E is influenced by impurities and by the state of ordering in an alloy, therefore, the agreement at room temperature of Δc with γT for the alloys not ferromagnetic at that temperature should be regarded as sufficiently good to conclude that γ does not change appreciably up to room temperature. Therefore, the high values of γ should not be due to the magnetic transformation.

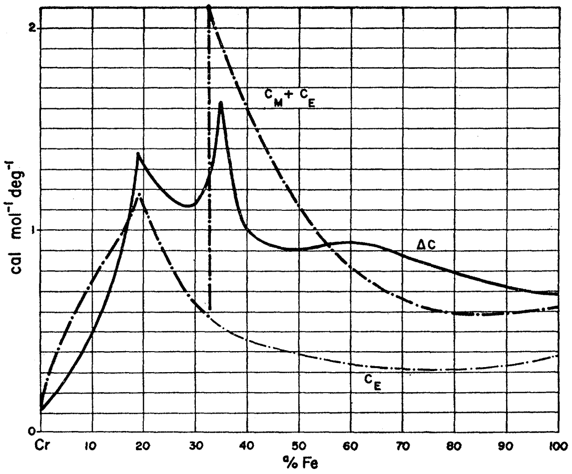

FIG. 2. Specific heat at room temperature vs composition; calculated electronic specific heat: $c_E=\gamma T$, (γ from reference 1), calculated magnetic plus electronic specific heat: c_M+c_E, lattice specific heat (taken as equal to that of Cr):c_L. $\Delta c=c_p-c_L-(c_p-c_v)$ is a quantity derived from the measured c_p, theoretically it should be equal to calculated c_M+c_E.

CONCLUSIONS

The large peak of the temperature coefficient, γ, of the term in the specific heat linear in temperature previously found[1] at 19 at. percent Fe by measurements at 1.5°–4°K is not due to the magnetic transformation, since the value of γ at the peak is approximately constant up to room temperature. It seems likely that the temperature coefficient may be interpreted in the usual way in terms of electronic specific heat.

ACKNOWLEDGMENTS

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[3] G. Pomey, Institut de Recherches de la Siderurgie Report, Ser. A-no. 117, November, 1955 (unpublished).

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[5] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand and Company, Inc., New York, 1951), p. 732.

[6] M. Fallot, Ann. phys. 6, 305 (1936).