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Specific Heat of Chromium-Rich Chromium-Nickel and Chromium-Iron-Molybdenum Alloys between 1.3 and 4.2 °K

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The specific heats of some chromium-based alloy systems were measured in the temperature range 1.3–4.2 °K. The alloy systems studied were the binary chromium-nickel with up to 4-at.% nickel and the ternary $Cr_{(0.75-x)}Fe_xMo_{0.25}$ with $0 \leq x < 0.20$. The electronic-specific-heat coefficient of the chromium-nickel system increases slowly with increasing nickel concentration and shows a maximum near 2-at.% Ni. The coefficients of the cubic temperature term in the specific heat of some of the binary alloys are relatively high. This observation was attributed to the effect of antiferromagnetic spin waves.

INTRODUCTION

The determination of the electronic band structure of the 3*d* transition elements has been the object of a great deal of study. Chromium alloys are particularly interesting because of their magnetic properties. Cheng *et al.*[1] investigated the specific heat of some of these alloy systems at liquid-He temperatures. They found that there was a rather large increase in the electronic-specific-heat coefficient γ_0 when one increases the electron concentration by adding iron. The Ti-Fe-Co system[2] provides similar evidence if γ_0 is plotted as a function of outer electron concentration, e/at. An average outer electron concentration per atom of 6.4 gave a maximum in γ_0.

This type of evidence tends to support a rigid-band model for the alloy system. However, if one observes the FeV system, one finds a peak in the electronic-specific-heat coefficient versus composition curve, but this peak has shifted from 6.4 to approximately 5.9 e/at.[1] Additionally the CrV system does not exhibit this anomaly in its composition range (5 to 6 e/at.).

The reason for the existence of these peaks is not at all clear. As a first guess one might associate this peak with the change from an antiferromagnetic to a ferromagnetic state. However, this assertion is not supported by the experimental data. Nevitt and Aldred's[3] magnetization data demonstrate that the Cr-Fe alloys with 18.2-, 19.4- and 20-at.% Fe are ferromagnetic and have Curie temperatures of 50, 70, and 81 °K, respectively. This extrapolates to a zero Curie temperature at a concentration of about 15-at.% Fe in Cr. However, the resistivity data of Rajan *et al.*[4] indicate that 16.1% Fe in Cr alloy is antiferromagnetic. This assertion is supported by the work of Schröder *et al.*[5] on the same alloy system. The magnetization measurements of Ishikawa and Tournier[6] conflict with this interpretation and indicate that the 15.2-at.% Fe in Cr sample is both superparamagnetic and superantiferromagnetic. Their work also asserts that the 4.6-at.% Fe in Cr alloy is superantiferromagnetic. The reason for this type of behavior is the short-range order of iron atoms. Hence, the differences in the measurements by these authors may be explained by the different thermal histories of specimens used in the various experiments which will lead to variations in short order. Additionally, the segregation of iron atoms could account for the unusual form of some of the specific-heat curves of Cheng *et al.*[1] which may possibly be explained by the addition of a constant specific-heat term due to clustering.[7] However, the important result that the density-of-states curve has a sharp peak for the *Cr*Fe alloys with 19 at.% is not contradicted with these experimental results. Specific-heat measurements between liquid-nitrogen temperatures and 350 °C[8] support the original findings by Cheng *et al.*,[1] especially if one keeps in mind that these measurements were done above the Curie temperature.

The transition in magnetic properties certainly does not explain the unusual behavior of the Cr-Mn system since all these alloys are antiferromagnetic. Low-temperature specific-heat measurements indicate, that the electronic-specific-heat coefficient γ_0 increases rapidly with increasing Mn concentration. c_p values above liquid-nitrogen temperatures, both below and above the Nѐel temperature do not show such large γ values.[9, 10] Some models have been proposed to explain the existence of this peak[11–13] but these cannot be applied to all the alloy systems studied.

An additional contribution to the electronic specific heat may arise if the existence of impurities in chromium gives rise to the formation of virtual-energy states at or near the Fermi surface. This possibility was exemplified by some work on the optical properties of CrFe[14] and CrMn, CrV, and CrNi[15] done at this institution.

Chromium-iron alloys do not only have unusual electronic-specific-heat coefficients but also in some cases they exhibit abnormally low Debye temperatures. This is shown by the 10- and 16-at.% Fe in Cr alloys which have Debye temperatures of 236 and 235 °K, respectively.[1] There are no known elastic anomalies in these alloys which would account for this and it may be possible that they are due to the complex magnetic structure of these alloys.

It is possible to avoid the complication due to the interaction of iron with an antiferromagnetic chromium matrix by substituting chromium with a chromium-molybdenum matrix. Heiniger *et al.*[16] showed that the chromium-molybdenum alloys with 25-at.% molybdenum or more are paramagnetic at liquid-He temperatures. The antiferromagnetism of chromium is not associated with localized moments but with conduction electrons and the peculiar Fermi surface of this element. Therefore, $Cr_{1-x}Mo_x$ with $x = 0.25$ should be a simple paramagnetic alloy system over the complete temperature range. We know of no complete ternary diagram for this system. The binary phase diagram indicates that molybdenum and iron form complete series of solid solutions with chromium and it was felt that this would overcome the poor solubility of molybdenum in iron.[17]

Hence, it was decided that the electronic properties of chromium alloys with an e/at. ratio between 5 and 6 might be further elucidated by studying the low-temperature heat capacity of some $Cr_{0.75-x}Mo_{0.25}Fe_x$ ternary and some Cr-Ni binary alloys, since the ferromagnetism in nickel is described with a collective electron interaction, not with localized moments as in pure iron.

EXPERIMENTAL PROCEDURE

The alloy samples were prepared by melting the pure element chips in a small cold mold arc furnace, under an inert argon atmosphere. The specimens were then annealed for 2 h at 1200 °C in a 92%-helium, 8%-hydrogen atmosphere and quenched.

The samples were weighed before and after the melting and annealing. The relative weight loss was in the order of $\frac{1}{2}$% for the annealed ingots. Some of the samples were sent out for wet analysis and all these agreed within ($\frac{1}{2}$%) of the nominal composition calculated from the in-weights. Spectrographic analysis showed the following impurities: Si (0.05%), Cu (0.05%), and traces (less than 0.01%) of Al, Co, Fe (in nickel alloys), Ni (in Fe alloys), Mg, K, Na, Mo, Li, and W.

Previous work done by the authors[18] showed the existence of a second phase in the Cr-Ni system. This second phase was present in the alloy samples with more than 6-at.% Ni. Hence, only the sample with up to 4 at.% were chosen for the experiments.

The heat capacities were then determined in the temperature range 1.3–4.2 °K. The samples were attached to a copper disc with an "evanohm" wire heater. In order to ensure that the germanium resistance thermometer was insulated from the disc but in good thermal contact with the specimen, a relatively large axial hole was cut in the disc. The thermometer was then mounted in this hole in good thermal contact with the sample, but with poor contact to the heater. The heat flowed to the thermometer via the sample. Good thermal contact was ensured by abrading a 62.5%-In, 21.5%-Ga, and 16%-Sn liquid-metal alloy into the surfaces of the disc, thermometer, and the samples. The heating current varied from 0.2 to 1 mA, and the heating time varied between 0.2 and 4 sec. The time of the heat pulse was determined by using a Berkeley timer.

It was felt that the utilization of He-3 as an exchange gas would eliminate the previously observed problem[1] of the "reevaporation of absorbed He-4 gas." However, this was not the case and the same or a similar problem was found with He-3 exchange gas used in our experiments. Experimentally, the problem was overcome in the same way as in previous experiments with He-4 as exchange gas, namely, by first cooling the system to 1.3 °K and then drawing a vacuum (less than 1 μm of Hg) on the specimen chamber. Then the specimens were heated to a temperature greater than 4.2 °K and allowed to cool back down to 1.3 °K.

The germanium resistance thermometer was calibrated by comparing its resistance with the vapor pressure of liquid helium which was condensed in the specimen can. The calibration changed slightly during the period that all the experiments were undertaken. This deviation was accounted for in the determination of the temperature and the change in temperature.

The values of the resistance obtained from the thermometer calibrations were fitted to the curve:

$$1/T = A \ln R + B/\ln R + C \tag{1}$$

in the temperature ranges 1.3–3.6 and 3.0–4.2 °K. A weighted average was used to determine the temperature in the overlap region. The above procedure gave values which fitted the temperature calibration to within $\frac{1}{2}$%.

A very simple Dewar system consisting of two strip-silvered wide-mouth glass Dewars was used for the experiments. The smaller Dewar, which contained the liquid helium, was encased in a long Pyrex tube, which was closed at one end (Fig. 1). The other end of the Pyrex tube extended well out

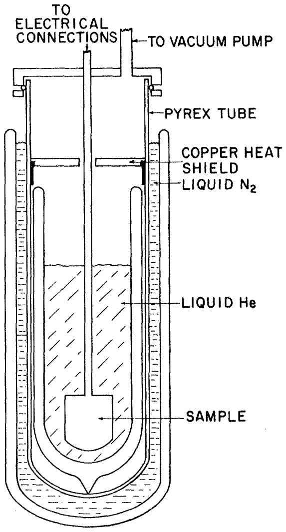

FIG. 1. Cryostat for liquid-He temperature measurements.

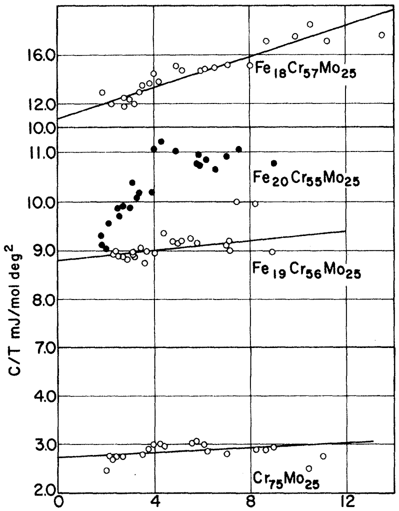

FIG. 3. Specific heats of chromium-molybdenum-iron alloys between 1.3 and 4.2 °K. Note change in scale for the alloy with 18-at.% Fe. Data for the alloy with 20-at.% Fe cannot be meaningfully correlated with Eq. (2).

of the insulating liquid-N_2 bath. The vacuum connections were made to this end and were thus kept at a temperature near room temperature. The liquid-He consumption was about 4 liter per experiment.

RESULTS AND DISCUSSIONS

The results for the heat-capacity measurements are given in Figs. 2 and 3. The heat capacities of all but one of the alloys ($Cr_{0.55}Mo_{0.25}Fe_{0.20}$) has a temperature dependence that may be expressed as

$$C = \beta T^3 + \gamma_0 T , \tag{2}$$

where γ_0 is the electronic-specific-heat coefficient of liquid-He temperatures. The βT^3 term is usually attributed to the lattice only. In that case, β is equal to $234R(T/\Theta)^3$. R is the gas constant and Θ^* is the apparent Debye temperature. The values of the electronic specific coefficient and of Θ^* are listed in Table I.

The scatter in the data is of the order of 5–10% depending upon the chosen alloy. It should be noted that there is an apparent correlation between the amount of scatter and the solute concentration. Generally, the scatter increased with increasing nickel concentration. Since microscopic examination did not reveal any cracks, this effect should be attributed to the increased thermal resistivity of the specimens. However, the values of γ_0 and Θ^* were reproducible to within 4%. Other published results on pure chromium[1] and chromium-

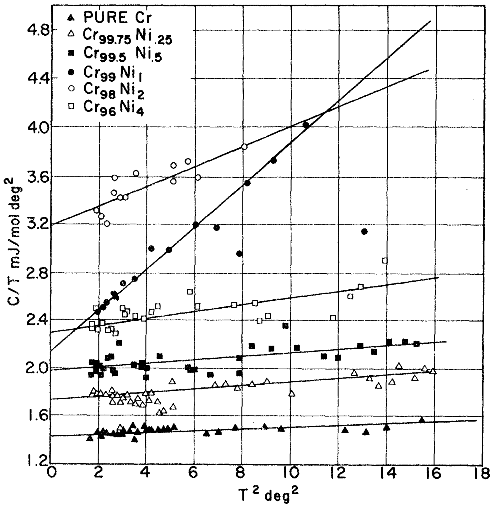

FIG. 2. Specific heats of chromium-nickel alloys between 1.3 and 4.2 °K.

TABLE I. Electronic-specific-heat coefficient (γ_0) and apparent Debye temperature (Θ^*) for the studied chromium alloys.

Alloy	γ (mJ/mole deg^2)	Θ^* (°K)
Cr	1.42	570
$Cr_{0.9975}Ni_{0.0025}$	1.74	506
$Cr_{0.995}Ni_{0.005}$	1.98	506
$Cr_{0.99}Ni_{0.01}$	2.29	228
$Cr_{0.98}Ni_{0.02}$	3.13	280
$Cr_{0.96}Ni_{0.04}$	2.15	465
$Cr_{0.75}Mo_{0.25}$	2.75	495
$Cr_{0.57}Fe_{0.18}Mo_{0.25}$	8.8	325
$Cr_{0.56}Fe_{0.19}Mo_{0.25}$	10.8	144
$Cr_{0.55}Fe_{0.20}Mo_{0.25}$	...	...

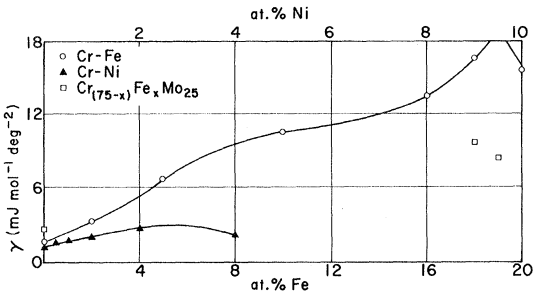

FIG. 4. Electronic-specific-heat coefficient for several chromium alloys. Data by Cheng *et al.* are given as open circles.

molybdenum alloys[16] are in good agreement with those listed in Table I. The review article[16] gives a γ_0 value of 1.41 mJ/mole deg^2 for pure chromium, and 2.7 mJ/mole deg^2 for the alloy with 25-at.% molybdenum, whereas our measurements gave $\gamma_0 = 1.42$ mJ/mole deg^2 for chromium and 2.75 mJ/mole deg^2 for the $Cr_{0.75}Mo_{0.25}$ alloy.

The values of the electronic-specific-heat coefficient versus composition are plotted and these are compared with previous work by Cheng *et al.*[1] on the chromium iron system in Fig. 4. It is obvious that a simple rigid-band model is not applicable to these alloys, since γ_0 plotted as a function of the "electron-per-atom" ratio follows different lines. As opposed to the chromium-iron and chromium-manganese case, there is no radical increase indicated in the electronic-specific-heat coefficient with increasing electron-per-atom ratios. In the case of chromium nickel only a weak maximum is found near 2-at.% Ni. The reason for the rather substantial difference between the *Cr*Ni and the CrFe systems is not completely clear. Most likely it should be attributed to the assertion that ferromagnetism of iron is due to localized electrons, whereas the ferromagnetism of nickel is described with a collective electron model. All the *Cr*Ni data fit Eq. (2). This differs somewhat from the results obtained from alloys studied by Cheng *et al.*,[1] where some of these data exhibited an upward curvature in the C/T plot. It does not seem possible to explain this peak in $N(E)$ by the Schottky (hyperfine) effect or with Einstein harmonic-oscillator model.

The experiments on $Cr_{0.75-x}Mo_{0.25}Fe_x$ alloys yield rather high γ_0 for electron-per-atom ratios close to 6.36. This is the electron concentration which yields a maximum γ_0 for Cr-Fe alloys. Since the Cr-Mo matrix of our alloys is not antiferromagnetic, the high γ_0 of the Cr-Mo-Fe alloys cannot be attributed to antiferromagnetic short-range order. One should therefore expect that possible magnetic long-range order in $Cr_{0.75-x}Mo_{0.25}Fe_x$ and $Cr_{1-x}Fe_x$ are different. Therefore, the large γ_0 values of both of these alloy systems are more likely due to purely electronic effects.

The apparent Debye temperature of some of the alloys is quite low. In the chromium-nickel alloys this is evident for the samples with 1 and 2% Ni which have apparent Debye temperatures of 228 and 280 °K, respectively. It should be noted that the (listed) values for the chromium-iron alloys[1] are all between 300 and 700 °K except for the 10- and 16-at.% alloys. These alloys have Debye temperatures of 236 and 235 °K, respectively.

If one looks for similarities in the above alloys with unusual Debye temperature, one can note that the temperatures at which the 10-at.% Fe alloy becomes antiferromagnetic is approximately 150 °K. The Néel temperature for the 2% nickel alloy is also approximately 150 °K as shown by the resistivity curves.[18] The Néel temperature is indicated by the minimum in the resistivity-versus-temperature curves. This supposition is supported by the interpretation of absolute Seebeck-coefficient data of these alloys, which have a minimum at T_N if plotted as a function of temperature.[5]

Since these alloys with similar Néel temperatures show similar anomalies in their specific heats, one is tempted to attribute the low "apparent" Debye temperatures to antiferromagnetic effects. Van Kranendonk and Van Vleck[19] proposed a model for the contribution to the heat capacity due to the spin waves in an antiferromagnet. Their model, based upon the analogy to harmonic oscillators, proposed that the spin-wave contribution to the specific heat of an antiferromagnet C_{SW} would have the following form:

$$C_{SW} = \frac{4R}{15}\left(\frac{kT}{2JS(2Z)^{\frac{1}{2}}}\right)^3 \qquad (3)$$

for cubic lattices. R is the ideal gas constant, k is Boltzmann's constant, Z is the number of nearest neighbors, S is the total spin number, and J is the exchange integral.

Hence, for an antiferromagnetic spin wave, the contribution was proportional to T^3 and inversely proportional to $(JS)^3$. The proportionality to T^3 will add to the lattice contribution since it is also proportional to the same factor. The term JS may be estimated by the Bethe-Peierls-Weiss method[20] or the series expansion method.[21] Both of these methods yield the result that the product JS is of the order of kT_N, where T_N is the Néel temperature. Thus one may observe that the spin-wave contribution to the specific heat of an alloy may be qualitatively expressed as being inversely proportional to the cube of the Néel temperature of that alloy. For this reason, alloys with 0-, 1.4-, and $\frac{1}{2}$-at.% Ni may have very low C_{SW} contribution at liquid-He temperatures. The other alloy included, namely, the 16-at.% Fe in Cr, as explained in the Introduction, may or may not be antiferromagnetic.[6] One should recall that the magnetic properties of the alloys are probably rather complex and strongly dependent upon the method of sample preparation. It is therefore not possible to show that C_{sw} is responsible for the low apparent Debye temperature in this alloy.

The low apparent Debye temperature of the ternary alloys cannot be explained with a spin-wave specific-heat contribution from Eq. (3) since it is very unlikely that these alloys are antiferromagnetic. It is more likely, that the simple analysis of Eq. (2) fails, because other terms than electronic, antiferromagnetic spin-wave, and lattice contribution have to be taken into account. The unusual form of the $\mathrm{Cr_{0.55}Fe_{0.20}Mo_{0.25}}$ curve supports this supposition.

There does exist the possibility that these alloys contain precipitates of unknown properties responsible for the anomalies of the specific heat. To investigate the microstructure of these alloys, x-ray diffraction studies were performed on a General Electric XRD-5 diffractometer. A chromium tube was used as the x-ray source. The results of this investigation of the ternary alloys were quite unusual. A scan of the possible diffraction angles for these alloys exhibited peak traces that could not be associated with the normal bcc, fcc, hcp, or tetragonal lattice structure. The increased suspicion of the possibility of a precipitate forced a thorough metallographic examination of the alloys. The problem was to find the proper etching reagent. After trying a number of different possibilities, "Vilella's" reagent (1-g picric acid, 100-mliter alcohol, and 5-mliter hydrocholoric acid) was used electrolytically.[22] Microscopic examination showed the presence of needlelike precipitates on the grain boundaries of the $\mathrm{Cr_{0.55}Mo_{0.25}Fe_{0.26}}$ alloy. The $\mathrm{Cr_{0.57}Mo_{0.25}Fe_{0.18}}$ and the $\mathrm{Cr_{0.56}Mo_{0.25}Fe_{0.19}}$ alloys also exhibited the presence of these precipitates, but to a much lesser degree (there was no observed precipitation in the $\mathrm{Cr_{0.75}Mo_{0.25}}$ alloy). The unusual specific heat of the ternary alloys may be due to these precipitates.

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