Review of the electronic specific heat of B. C. C. and F. C. C. solid solutions of first long period transition elements

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REVIEW OF THE ELECTRONIC SPECIFIC HEAT OF B. C. C. AND F. C. C. SOLID SOLUTIONS OF FIRST LONG PERIOD TRANSITION ELEMENTS

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Résumé. — On passe en revue les résultats relatifs aux chaleurs spécifiques des solutions solides cubiques centrées, et certaines données nouvelles sur le système V-Cr et Ti-V. Les chaleurs spécifiques sont remarquablement bien décrites par un modèle de bandes rigides, même pour les mélanges ternaires.

En ce qui concerne les solutions solides cubiques à faces centrées, les valeurs de $\gamma$ mesurées ont une interprétation électronique simple seulement pour les alliages ferromagnétiques ou non magnétiques. Pour les alliages où coexistent des interactions ferro- et antiferromagnétiques, la valeur expérimentale de $\gamma$ paraît comprendre souvent une contribution magnétique. En se limitant aux alliages non magnétiques ou ferromagnétiques on peut déterminer la forme de la bande $d$ pour la structure cubique à faces centrées et pour des concentrations allant de 8 à 10 électrons $d$ par atome.

Abstract. — A review will be given of the electronic specific heat vs. electron concentration for b. c. c. solid solutions, including new data for the systems V-Cr and Ti-V. The latter alloys show a maximum of $\gamma$ at approximately 60 % V. The electronic specific heat coefficients correlate well the superconductive transition temperatures, according to the Bardeen-Cooper-Schiffer theory, with an interaction coefficient $V$ independent of composition. It was found that the CsCl-type ordered alloys in the ternary Ti-Fe-TiCo and TiCo-TiNi systems possess electronic specific heat values paralleling those for the b. c. c. Cr-Fe alloys at the same average electron concentrations. The electronic specific heat values for the b. c. c. alloys of transition elements with one another can be apparently described to a surprising extent in terms of a more or less rigid band, the degree of filling up of this band with electrons being determined essentially by the average electron concentration for the alloy. This appears to hold even in cases where the electron concentration is determined by averaging over three different atomic species. As found also for the alloy VFe, with a CsCl-type ordered structure, ordering causes little, if any, change in the electronic specific heat values of these alloys.

New low temperature specific heat measurements with f. c. c. solid solutions in the Mn-Fe, Mn-Ni, Fe-Ni, V-Ni systems gave coefficients for the specific heat term linear in temperature, which are in some cases quite inconsistent with each other if interpreted as electronic specific heat coefficients. Consistent $\gamma$ values were obtained for simple ferromagnetic alloys and for non magnetic alloys. For alloys where the simultaneous presence of both ferromagnetic and antiferromagnetic interactions is known from magnetic measurements, or may be considered as very likely, the measured $\gamma$ values are anomalously high. It has been proposed by Marshall (1) that a temperature-linear contribution to the low temperature specific heat can arise in instances where a sufficient number of spins are located in a near zero magnetic field. It appears from our results that this condition is often fulfilled in alloys having both ferromagnetic and antiferromagnetic interactions. As a result, in such cases the $\gamma$ value measured at low temperatures comprises, in addition to the true electronic specific heat coefficient, also a magnetic component. Using only $\gamma$ values obtained for simple ferromagnetic and for nonmagnetic alloys, the shape of the $d$-band for the f. c. c. solid solutions has been nevertheless successfully determined in the electron concentration range from approximately 8 to 10.

In a previous paper [1] electronic specific heat vs. electron concentration data were published for b. c. c. solid solutions of first long period transition elements. Measurements made recently [2] with b. c. c. solid solutions in the Ti-V system confirm the peak in the electronic specific heat predicted [1] for these alloys [4]. Figure 1 shows the combined electronic specific heat data for the b. c. c. alloys in the entire electron concentration range where solid solutions with this structure are formed by the transition elements of the first long period.

The second high peak of $\gamma$ corresponds roughly to the onset of ferromagnetism in the Cr-Fe alloys ; the question arises as to whether this peak may be of magnetic origin. The high temperature specific heat data of Schrôder [5] clearly indicate (fig. 2), that the large peak in the term of the low temperature specific heat linear in temperature, which occurs at around Cr + 19 % Fe is not of magnetic origin, but that it is indeed an electronic specific heat coefficient.
It was recently found [6] that the CsCl-type ordered alloys in the ternary TiFe-TiCo and TiCo-TiNi systems have electronic specific heat values paralleling very closely those for the b.c.c. Cr-Fe alloys at the same average electron concentrations (fig. 3). These results represent further confirmation of the electronic specific heat nature of the measured $\gamma$ values. They also underline the surprising extent to which the electronic specific heat of the body centered cubic alloys of transition elements with one another can be interpreted in terms of a more or less rigid $d$-band, the degree of filling up of this band with electrons being determined by the average electron concentration of the alloy. This is now shown for ternary alloys, where the electron concentration is determined by averaging over three different atomic species. Ordering apparently makes little, if any, difference in the electronic specific heat. This is not very surprising in view of the work of Rayne [7] with AuCu$_3$. Also, newer results for VFe with a CsCl-type ordered structure [8] show the electronic specific heat to be nearly the same as that for the disordered alloy of the same composition.

The density of states vs. energy, calculated from the data given in figure 1 according to the method of Hoare [9], is given in figure 4, where the density of states vs. energy in eV for the $d$-electrons. Zero of energy scale corresponds to Cr.
of states for the two spin directions is plotted separately. The interpretation presented in the figure makes use of magnetic saturation moment data for these alloys as shown in the Slater-Pauling curve [7], and of neutron diffraction data [12]. The combination of these data with the electronic specific heat results clearly indicates that the first sub-band, lying in the electron concentration range between 4 and 6 (fig. 1) or in the energy range between -$1.2$ and $0$ eV (fig. 4), represents an equal number of electrons with positive and with negative spin direction, since the alloys in this range have no net permanent moment. The second sub-band, which extends over the electron concentration range from about 5.8 to 8.4 (fig. 1) or in the energy range from $-0.4$ to $+1.35$ eV (fig. 4), clearly represents electrons in one spin orientation only. The atomic moments, as measured by saturation magnetization or by neutron diffraction, correspond to the number of electrons added to this sub-band. The fractional saturation moment of Fe (2.2 $\mu_B$) can now be understood as a result of the fact that the second sub-band begins at an electron concentration of approximately 5.8, and that all the electrons added to this sub-band contribute to the moment.

Although the above model is consistent with the known experimental facts, it certainly does not fit the usual concept of the structure of the d-band of Fe. In the usual picture, Fe is considered to have both + and − spin orientations at the Fermi surface [13] while the above discussed results suggest [1] that in Fe there should be d-electrons at the Fermi surface with one spin orientation only. Recent measurements by Walmsley [14] of the change in the contact potential between Fe and Cu on applying an external magnetic field gave a direct confirmation of this concept. Walmsley also established that the sign of spin of the d-electrons at the Fermi surface in Fe is positive.

Finally, the third sub-band, extending from approximately 8.2 electrons per atom to the end of the range of stability of the b. c. c. structure at around 8.7 electrons per atom (fig. 1) or from $+1.06$ to $+1.64$ eV (fig. 4), represents electrons with the opposite spin direction only, as shown by the decreasing saturation moment with increasing number of electrons per atom (Slater-Pauling curve).

The separation of the positive ("second") and negative ("third") sub-bands here is approximately 1.5 eV. This value is much larger than the exchange energy associated with the Curie temperature. Since $T_c <$ 1 000 °K for all of the alloys concerned, the latter exchange energy $kT_c < 0.1$ eV.

The observed separation, which is at least an order of magnitude larger, must correspond instead to the much larger intra-atomic exchange energy which gives rise to (unaligned) atomic moments well above the Curie temperature.

It is interesting to compare the electronic specific heat results with magnetic susceptibility data for some of the same alloy systems, published recently by Taniguchi, Tebble and Williams [15]. Comparison of figure 5 with figure 1 shows the expected parallelism at least in the electron concentration range between 5 and 6.5. (For the V-Cr alloys this was already found earlier by Childs, Gardner and Penfold [16].) However, the $\chi$ and the $\gamma$ vs. composition curves differ from each other very significantly for the Ti-V alloys. The magnetic susceptibility of Ti-Nb alloys also varies in a manner similar to that of the Ti-V alloys in the same electron concentration range, as shown by Jones, Pessall and McQuillan [17]. The reality of the difference between the variation of $\chi$ and of $\gamma$ can not be doubted, but its explanation is, at present, unknown.

Low temperature specific heat measurements have been made with f. c. c. solid solutions in the Mn-Fe, Mn-Ni, Fe-Ni, and V-Ni systems [20]. The resulting coefficients of the low temperature specific heat term linear in temperature, if interpreted as electronic specific heat coefficients, are in several cases quite inconsistent with the rigid band model. As seen in figure 6, the $\gamma$ values obtained by Walling and Bunn [18] for f. c. c. Co-Ni solid solutions, which are strongly ferromagnetic, are in reasonably good agreement with the values obtained by Keesom and Kurrelmeyer [19] and in this laboratory [20] for f. c. c. Fe-Ni alloys in the same electron concentration range. These Fe-Ni alloys are also strongly ferromagnetic. The value of $\gamma$ for ordered MnNi$_3$, as reported by Goldman [21],
is also fairly close to that of the Co-Ni solid solution at the same electron concentration (fig. 6). It is known that ordered MnNi₃ is also ferromagnetic, with a Curie temperature of 475 °C [22].

![Graph](image)

Fig. 6. — \( \gamma \) vs. electron concentration for f. c. c. alloys in the Mn-Fe, Mn-Ni, Fe-Ni, Co-Ni and V-Ni systems. For MnNi₃, \( \gamma \) is given for the following conditions: disordered (symbol ⋄), short-range ordered (symbol ⋄-), and long-range ordered (symbol ⋄C). For Fe₃Ni, \( \gamma \) was determined after cooling in a magnetic field (symbol 0), as well as without magnetic field (symbol ⋄) [20].

However, the \( \gamma \) value reported by Goldman [21] for disordered MnNi₃ is very much higher. This result was recently confirmed [20]. (See the two nearly coinciding ⋄ symbols in figure 6). Dreesen concluded from his study of the effect of order on the Hall constant of MnNi₃ [23] that the observed difference in the \( \gamma \) values between ordered and disordered MnNi₃ is not a result of a change in the band structure upon ordering. This conclusion is supported by all results obtained to date on the effect of ordering on the electronic specific heat of alloys having no magnetic moments [7, 8]. This raises the question why the coefficient of the low temperature specific heat term linear in temperature increases upon ordering in the case of MnNi₃. Overhauser first proposed a theory [24] for a low temperature specific heat term of magnetic origin, which is linear in temperature. This theory postulates that a large number of spins are located in a near zero field as a result of the presence of stationary spin waves in an antiferromagnetic structure. In view of the fact that disordered MnNi₃ is ferromagnetic [22], it appears that Overhauser's theory could not be applied to it. On the other hand, Marshall's theory [25] is also based on spins located in near zero field, does not require antiferromagnetic structure. It appears very probable that the increment of the observed \( \gamma \) value for disordered MnNi₃ over that of ordered MnNi₃ is a result of the mechanism described by Marshall [25] and that the condition of spins located in near zero average field is satisfied in the disordered MnNi₃ alloy as a result of its peculiar magnetic structure. It is known from the work of Kouvel and Graham [26] that this alloy shows "exchange anisotropy" when cooled through the magnetic transformation temperature range in a magnetic field. The observed unusual magnetic effects result from the presence in this material with an overall ferromagnetic structure of locally antiferromagnetic spin arrangements. It has been suggested by Kouvel [27] that in the Cu-Mn and Ag-Mn alloys, which also show "exchange anisotropy", the simultaneous presence of ferromagnetic and antiferromagnetic interactions on an atomic scale is a result of the statistical variations in the separation of pairs of near Mn atoms, and of the strong dependence of the type of exchange coupling between Mn pairs on the distance of separation. It is extremely likely that the same mechanism accounts also for the exchange anisotropy observed in disordered MnNi₃. Consequently, it is reasonable to assume that many atomic moments in this alloy are located in a near zero average local field resulting from the near compensation in these local areas of the ferromagnetic and antiferromagnetic exchange interactions. It may be expected, therefore, that the condition required by Marshall's theory is satisfied. In order to test the above hypothesis, an MnNi₃ alloy specimen, which had been disordered by annealing at 1 000 °C and preserved in this condition by quenching, was re-annealed for two hours at 485 °C, in order to achieve short range ordering and thus to decrease the number of nearest neighbor Mn pairs, which presumably give rise to local antiferromagnetic coupling. This heat treatment was selected on the basis of results reported by Marcinkowski and Brown [22]. As seen in figure 6, the measured \( \gamma \) value after this heat treatment (symbol ⋄-) was considerably lower than that in the disordered condition. In the case of disordered MnNi₃ the magnetic component of \( \gamma \) approximately doubles the apparent "electronic specific heat". However, the magnitude of this extra specific heat decreases rapidly with increasing Mn-content. It may be seen in figure 6 that the curve corresponding to Mn-Fe alloys is crossed by the corresponding curve for the Ni-rich Fe-Ni alloys. The measured \( \gamma \) values for the latter alloys at high Fe-contents become extremely large. The question should be considered next whether or not these very high \( \gamma \) values may also comprise large magnetic contributions. The magnetic properties of the Fe-rich f. c. c. Fe-Ni alloys have been investigated by Kondorskii and Fedotov [28] who found that, superimposed on the overall ferromagnetic
structure, a latent antiferromagnetism must be assumed in order to account for the measured macroscopic magnetic properties. Consequently, it may be assumed that, for these disordered alloys, as well as for the disordered f. c. c. Mn-Ni alloys, the condition required by Marshall’s theory may be satisfied in the manner here proposed. In order to test this model, the alloy containing 30 % Ni (and also 5 atomic per cent C to stabilize the f. c. c. structure) was cooled in a magnetic field of approximately 10 kG from 400 °C to room temperature. After this heat treatment the specimen was again introduced into the calorimeter and its low temperature specific heat was measured. As seen in figure 6 (symbol C) the heat treatment increased the measured γ value. The observed effect of magnetic cooling suggests strongly that this alloy also exhibits exchange anisotropy, and that the measured γ value comprises a magnetic contribution. The crossing of the curves for Mn-Ni and Fe-Ni alloys in figure 6 thus turns out to be of no particular significance, since there is no reason to expect that the peculiar spin arrangement giving rise to the large magnetic contribution to γ should occur in different alloy systems at the same electron concentration.

A similar lack of consistency may be observed in figure 6 between the γ values for Mn-rich Mn-Ni alloys and Fe-rich Mn-Fe alloys. The fact that γ is unusually large for a f. c. c. Fe + 11 % Mn alloy has been reported earlier by Goldman [29], and the much lower γ value for Fe + 45 % Mn was also known [30]. Corliss and Hastings found [31] that the observed magnetic moments of non-magnetic V-Ni solid solution alloys were also measured. As seen in figure 6, the measured γ values for the non-magnetic alloys represent a reasonable extension of the curve for the “purely” ferromagnetic Co-Ni and Fe-Ni alloys (no “latent antiferromagnetism”). The magnetic contribution to γ discussed above, which occurs in alloys having both ferromagnetic and antiferromagnetic interactions, is absent for both of these cases. Consequently, it seems justifiable to propose that the true electronic specific heat of the f. c. c. alloys in the electron concentration range between 8 and 10 may be represented approximately by the heavy line in figure 6. The points for the two Mn-Ni alloys near the equiatomic composition are also near this curve.

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REFERENCES

[8] Vanreuth (E. C.), Cheng (C. H.) and Beck (Paul A.), to be published.
[16] Childs (B. G.), Gardner (W. E.) and Penfold (J.), Phil. Mag., 1960, 5, 155.
[17] Jones (D. W.), Fessall (N.) and Mcquillan (A. D.), Phil. Mag., 1961, 6, 455.
Ferromagnetic Properties of Fe and Ni in Relation to Their Band Structure

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Résumé. De nombreuses propriétés de Fe et Ni peuvent être reliées les unes aux autres au moyen d’une théorie empirique supposant que le moment atomique magnétique n’est pas constant dans les métaux de transition mais est supposé dépendre dans ces cas de la température, du volume et du champ magnétique externe.

Les propriétés en question sont, parmi d’autres, la magnétostriction en volume dépendant du champ, la variation de magnétisation et du point de Curie avec la pression et les déviations par rapport aux courbes de Brillouin de la magnétisation à saturation en fonction de la température.

Les variations du moment atomique magnétique sont estimées en incorporant les moments magnétiques localisés dans la théorie des bandes pour les électrons 3d.

Abstract. Several properties of the elements Fe and Ni can be correlated with each other by means of an empirical theory, which assumes that the atomic magnetic moment does not have a constant value in transition metals, but is thought to depend in these cases on temperature, volume, and external magnetic field.

The properties in question are, among others, the field-dependent volume magnetostriction, the change of magnetization and Curie point with pressure, and the deviations of the temperature dependence of the saturation magnetization from the appropriate Brillouin curves.

Variations of the atomic magnetic moment are estimated by incorporating localized magnetic moments into the electron band theory of the 3d-electrons.

Some of the physical properties of iron metal display unexplained anomalies. We found that the field-dependent volume magnetostriction, h'O, does not disappear at low temperatures, but remains approximately constant. Moreover, the temperature dependence of the saturation magnetization deviates more than 10% from the theoretically expected Brillouin curve, while the value for the exchange energy as found from spin wave theory, differs considerably from the value, calculated from the experimentally determined Curie point.

In other ferromagnetics these properties give a better fit with theory.

These difficulties can be removed by considering the localized atomic magnetic moment, \( a \), of the atoms in a magnetic metal as a variable. This is in contradistinction to the moments in magnetic salts, which have fixed values that have been calculated. We assume that \( a \) is a function of temperature, volume, etc. For a certain value of \( a \), the energy will be a minimum; we assume a quadratic dependence of the energy upon \( a \) in the neighbourhood of this equilibrium value.

If we define \( a \) as the magnetic moment per atom expressed in Bohr magnetons, and \( \delta \) as a relative change in volume of the lattice, then the terms of the free energy per atom, \( F \), which depend on \( a \) or \( \delta \), can be written as:

\[
\frac{F}{N} = \frac{1}{2} k T \delta^2 + \frac{1}{2} k T (a - \langle a \rangle)^2
\]

The effects of lattice vibrations, causing the thermal expansion are omitted here. The first term gives the quadratic dependence of \( F \) on \( a \), which we have already mentioned; the second...