very well to the curve which has been measured directly in the accessible ferromagnetic region. The magnetic moment of the iron-rich γ-phase with Pd concentrations above 7% Pd has been calculated to be 4.2 Bohr magnetons per atom.

One must conclude that the iron-rich γ-phase of Pd alloys should be ferromagnetic at sufficiently low temperatures if they were stable at these temperatures. There is no indication for an antiferromagnetic coupling in the subcooled γ-phase in the immediate neighborhood of the invar alloys. Consequently, the characteristic (c) mentioned above seems to be no necessary condition for the existence of an invar effect.

References

1 Y. Tino: J. Sci. Res. Inst. **47** (1952) 141.
2 U. Dehlinger: Z. Metallkunde **28** (1936) 194.
3 E. I. Kondorsky and V. L. Sedov: J. Appl. Phys. **31** (1960) 331S.

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The Paramagnetic Susceptibility of Some b.c.c. Transition Element Alloys and Its Temperature Dependence

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The paramagnetic susceptibilities of some b.c.c. transition metal alloys have been measured in the temperature range between 20° and 1350°C. The observed curve of χ_{20} (the room temperature susceptibility) against q (number of outer $d+s$ electrons) has been found to be binodal and similar for the first, second and third series alloys. The susceptibility is a maximum for $q\sim5$ and a minimum at slightly less than 6. The temperature dependence of susceptibility for alloys measured is as expected from the band model assuming that the shape of the density of state curve follows the $(\chi_{20}-q)$ curve.

The susceptibility and its temperature dependence of the h.c.p. phase have been found to be quite different from those of the b.c.c. phase of the same composition. A possible shape for the density of state curve of the close packed structure is also proposed based on the present study and the available data.

The paramagnetic susceptibilities of b.c.c. Ti-V, V-Cr, Cr-Mn (up to 50% Mn), Zr-Nb, Nb-Mo, Hf-Ta, Ta-W, Ta-Re (up to 37.5% Re) and Nb-Ta alloys have been measured in the temperature range 20° to 1350°C by means of a Sucksmith ring balance.¹⁾ Most of the raw materials used for the preparation of the alloys were the spectrographically standardized substances supplied by Johnson, Matthey and Co., and they were melted in an argon-arc furnace. Except for Ta-Re and Nb-Ta alloys, these alloys are the solid solutions of neighboring transition elements in the same series in the periodic table.

The observed room temperature suscepti-

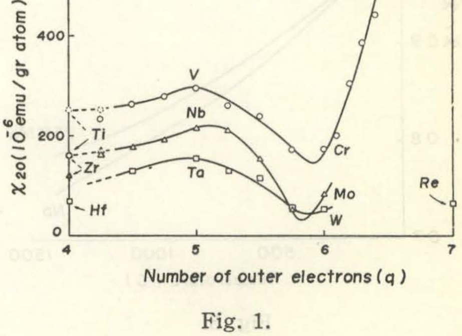

Fig. 1.

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bilities χ_{20} are plotted in Fig. 1 against the number of outer $s+d$ electron concentration, q. The χ_{20} *vs* q curves for the first, second and third series alloys are similar to each other and they are maximum at about $q=5$ and minimum at slightly less than 6, respectively. It is to be noted that the relative variation of susceptibility is largest in the second series alloys.

The observed temperature coefficient of susceptibility is negative in the alloys near the maximum of χ_{20} *vs* q curve while it is positive in the alloys near the minimum.

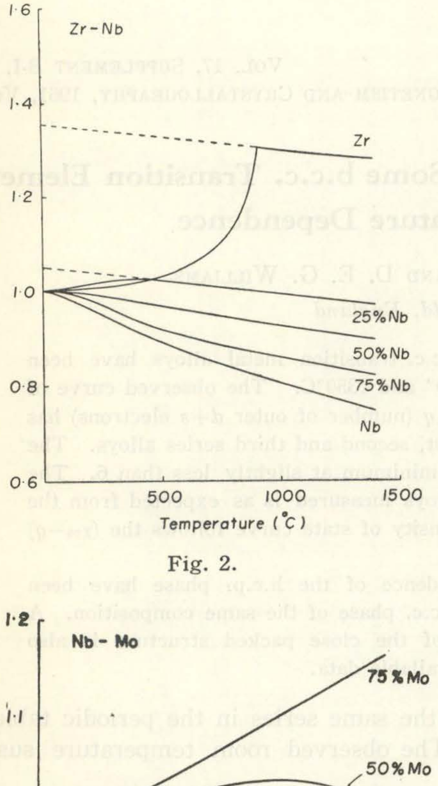


Fig. 2.

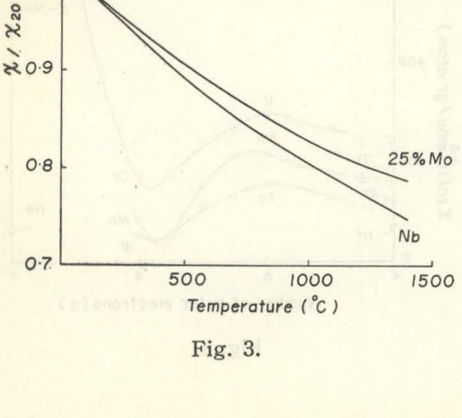
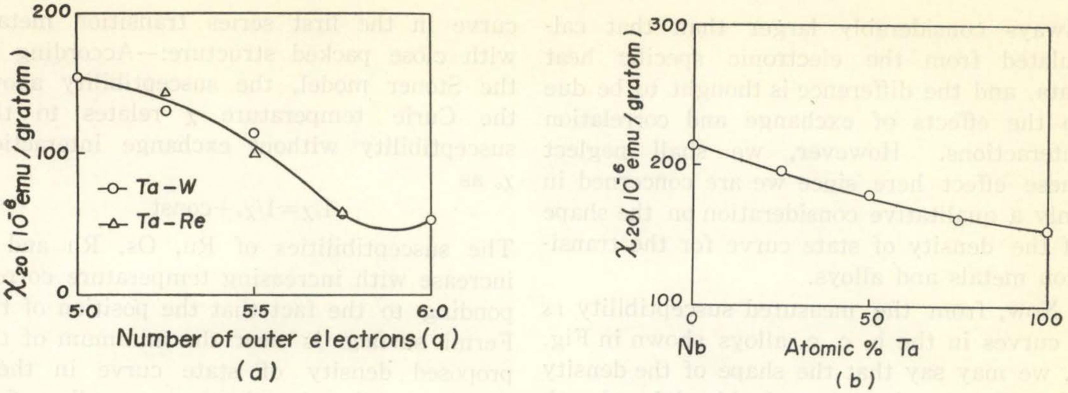


Fig. 3.

For example, the temperature dependence of susceptibility in the second series alloys, Zr-Nb and Nb-Mo, is shown in Fig. 2 and 3, respectively. The susceptibilities of pure Zr and 25% Nb alloy increase with increasing temperature at first, but they decrease in the high temperature region similarly to the high Nb alloys. The negative slope increases with increasing Nb content. Pure Zr and 25% Nb alloy are h.c.p. structure and transform to the b.c.c. structure at high temperature. The extrapolated susceptibility values for b.c.c. Zr and 25% Nb alloy at room temperature are plotted by the dotted triangles in Fig. 1 and they fit well into the χ_{20} *vs* q curve. Similar facts have been found also in the first series Ti-V alloys. In this way, both the magnitude and the temperature dependence of susceptibility in the h.c.p. phase are quite different from those in b.c.c. phase, indicating an appreciable influence of a lattice type on the electronic structure of transition metals and alloys. The temperature coefficient of susceptibility changes from negative to positive with an addition of Mo to Nb as shown in Fig. 3, and 75% Mo alloy has a larger temperature coefficient than pure Mo corresponding to the fact that the former is nearer to the minimum in the χ_{20} *vs* q curve. Such a correlation between the magnitude and the temperature dependence of susceptibility can be expected from the band model with an assumption that the shape of the density of state curve for these alloys is similar to the observed χ_{20} *vs* q curve.

However, before we consider the shape of the density of state curve based on the susceptibility data, the effects of alloying and of exchange interaction have to be examined. For the examination of an effect of alloying, Ta-Re and Nb-Ta alloys have been measured. Re is the second series transition element next to W and has one more electron. The observed results on Ta-Re alloys were compared with those of Ta-W alloys with the same electron concentration and it was found that the magnitude and temperature dependence of susceptibility were quite similar to each other. The susceptibility data are shown in Fig. 4(a). Nb and Ta are the second and third series elements in the same column in the periodic table, that is, they



(a)

(b)

Fig. 4.

both have the same value of $q(=5)$, and the negative temperature coefficients. Both the magnitude and the temperature dependence of susceptibility change quite regularly from Nb to Ta indicating no appreciable influence of alloying on the relative position of the Fermi surface. The observed room temperature susceptibilities in Nb-Ta alloys are shown in Fig. 4(b). These facts seem to indicate that the effect of alloying on the electronic structure is very small, at least, in the alloys of neighboring transition elements in the same series in the periodic table and that the magnitude and the temperature dependence of susceptibility are primarily determined by the electron concentration alone.

The next problem for a discussion of the density of state curve based on the susceptibility data is an effect of exchange interaction. A neutron diffraction study has shown that 50% Mn-Cr alloy is antiferromagnetic at room temperature and that the Néel point is much higher than 300°C.[2] Pure Cr is also antiferromagnetic below about 40°C.[3] However, no pronounced susceptibility peak at the Néel point was found in any Cr-Mn alloy measured in the temperature range between 20° and 1050°C (Fig. 5). The temperature coefficient of susceptibility changes from positive for Cr to negative with an addition of about 20% Mn, and 50% Mn alloy looks very much like to follow the Curie-Weiss law even below the reported Néel temperature. These behaviours can be understood in terms of the band theory of antiferromagnetism developed by Slater and by Lidiard. According to the latter theory, in particular, the absence of or no pronounced susceptibility peak at the Néel point was attributed to a weakness of the relative magnetization in each of the sublattices. Then, the measured susceptibilities of Cr-Mn alloys have, roughly speaking, the same sense as those of the other paramagnetic alloys have. A rapid increase in the electronic specific heat has been also found in Cr-Mn alloys by Cheng, Wei and Beck.[6] Even in weakly para- or diamagnetic metals, the exchange and correlation effects between electrons must be taken into consideration for a detailed discussion of the susceptibility. In the transition metals, moreover, the observed susceptbility is

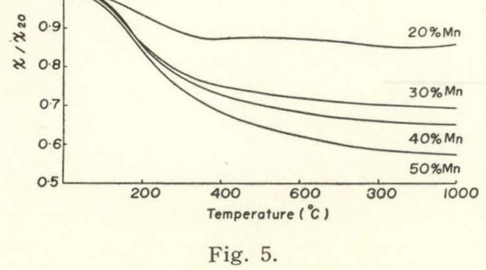


Fig. 5.

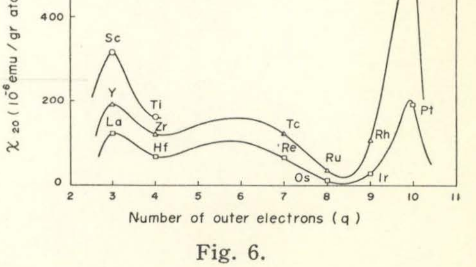


Fig. 6.

always considerably larger than that calculated from the electronic specific heat data, and the difference is thought to be due to the effects of exchange and correlation interactions. However, we shall neglect these effect here since we are concerned in only a qualitative consideration on the shape of the density of state curve for the transition metals and alloys.

Now, from the measured susceptibility *vs* q curves in the b. c. c. alloys shown in Fig. 1, we may say that the shape of the density of state curve is commonly binodal and each subband may involve about 5 electrons each.

The shape of the density of state curve for the close packed phase alloys might be quite different from that of b. c. c. phase alloys as seen from Fig. 2. Fig. 6 shows the collected room temperature susceptibility data of the transition metals with close packed structure available at present. The susceptibility *vs* q curves in the second and third series metals are similar to each other and they commonly have three maxima, two relatively high maxima at the top and at the bottom of the band and a flat maximum between the two. These proposed shapes of the density of state curve for the b. c. c. and close packed phase alloys are, to some extent, supported by the electronic specific heat data. However, one question arises for a use of such a shape of the density of state curve in the first series transition metals with close packed structure:—According to the Stoner model, the susceptibility above the Curie temperature χ relates to the susceptibility without exchange interaction χ_0 as

$$1/\chi = 1/\chi_0 + \text{const.} \qquad (1)$$

The susceptibilities of Ru, Os, Rh and Ir increase with increasing temperature corresponding to the fact that the position of the Fermi surface is near the minimum of the proposed density of state curve in these metals, while, in the corresponding first series transition metals, that is, in Co and γ-Fe, their susceptibilities decrease with increasing temperature. This is presumably due to the fact that the d electrons in a very high density band are not so free to move as the simple band model assumes.

References

1 H. Kojima, R. S. Tebble and D. E. G. Williams: Proc. Roy. Soc. **A260** (1961) 237.

2 J. S. Kasper and R. M. Waterstrat: Phys. Rev. **109** (1958) 1551.

3 L. M. Corliss, J. M. Hastings and R. J. Weiss: Phys. Rev. Letters **3** (1959) 211. R. H. Beaumont, H. Chihara and J. M. Morison: Phil. Mag. **5** (1960) 188. E. W. Collings, F. T. Hedgecock and A. Siddigi: Phil. Mag. **6** (1961) 155.

4 C. H. Cheng, C. T. Wei and P. A. Beck: Phys. Rev. **120** (1960) 426.

DISCUSSION

B. T. MATTHIAS: How come that your peak of the susceptibility does not coincide with Wei and Beck's data? They find a peak of the specific heat between Ti and V. Your peak is strictly at V. How do you explain this discrepancy, as both maxima, according to your hypothesis, ought to coincide?

S. TANIGUCHI: Our measurements were made on the alloys of 25% solute interval. We found that the susceptibility of 75% V-Ti alloy was lower than that of pure V. Dr. Gardner at Harwell found that the maximum of the susceptibility in Ti-V alloys is not at pure V but at about 5% Ti-V. As for the electronic specific heat data of Wei and Beck, they measured only one specimen between V and Ti, values of these metals being taken from literatures.