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THE TRANSITION IN CHROMIUM AND IN SOME ALLOYS
OF CHROMIUM WITH SMALL AMOUNTS
OF OTHER TRANSITION ELEMENTS

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Résumé. — On étudie le point de transition du chrome à 38 °C en mesurant l'influence de l'addition de petites quantités des autres éléments de transition (V, Mn, Fe, Co ou Ni) sur la résistance électrique et l'effet Hall. Les résultats prouvent la nature électronique de la transition.

Abstract. — The transition in chromium at 38 °C is investigated by measuring the influence on the electrical resistance and the Hall effect of alloying with about 1 at. % of V, Mn, Fe, Co or Ni. The results prove the electronic nature of the transition and give an indication of the identity of the 38 °C transition with the Néel point.

The antiferromagnetism of the pure chromium metal has, it seems, been rather a mystery ever since its discovery by Shull and Wilkinson [1]. Contrary to all known antiferromagnetic or ferromagnetic solids no other properties have been found that showed anomalies at 450 °K the reported transition temperature. On the other hand, at 38 °C many physical properties of chromium do show anomalies. The nature of the transition underlying these anomalies is by no means clear. One is tempted to identify this transition with the disappearance of antiferromagnetism. However no conclusive evidence has been presented in favour of this supposition [2, 3, 4].

In order to investigate this possibility a series of alloys with about one at. % of the transition metals V, Mn, Fe, Co, Ni, was prepared. The magnetic coupling of the chromium with the other metal may be expected to change the Néel temperature, just as, in the case of ferromagnetic alloys, the Curie temperatures. These alloys were prepared for us by Professor Fast of Eindhoven. The results of measurements of the resistivity and the Hall constant are shown in the figures. The curves for the pure chromium agree with the earlier measured values on ductile chromium that was supplied by Dr. Wain, Melbourne [5].

Some measurements were started on the magnetic susceptibility of the alloy. However the probable presence of Cr₂O₃ that has its Néel temperature at about 40 °C caused some difficulty.

In discussing our results it should be remarked first that Cr₂O₃ cannot be responsible for the anomaly found in Cr metal. Also a sample of in hydrogen at 1 400 °C purified Cr showed the same anomaly in Young's modulus as is reported by other authors [2, 4]. Another argument is found in the case of the Ni alloy where the transition temperature is shifted downwards considerably though Ni cannot be expected to enter the oxide.

Considering now the figures it is seen that V and Mn cause a very large shift in transition temperature respectively down to about — 50 °C, and up to about 190 °C. This would be expected for a Néel transition as V is not magnetic at all [1] and Mn in the body centred cubic structure probably would have a high Néel temperature [6].
It is somewhat difficult to reach similar conclusions in the case of the other metals that are farther removed from Cr in the periodic table of elements. (Compare the case of the ferromagnetic element Co alloyed with small amounts of Ni or Fe on the one hand, and Mn and Cr on the other hand.)

The effect of alloying on the Hall constant is very striking. There appears to be a correlation between the temperatures below which the Hall constant appears to rise strongly and the temperature at which the anomaly in the resistance occurs. This is especially clear in the case of the V and the Fe alloy. The Mn alloy that is still far beneath its transition point at room temperature also has the highest Hall constant there. All constants are positive and very large, though a factor 100 smaller than indicated in the figure. (Cu has a Hall constant of about $5.5 \times 10^{-11}$). The highest value measured for the Fe alloy corresponds to about one hole per 20 atoms. In this connection it must be reported that the antiferromagnetic alloy 85 % Mn 15 % Cu did not show a significant change of Hall constant at or near to the transition temperature.

These results prove the transition to be of an electronic nature; whether it is the Néel temperature or not, can only be solved by further experiments.

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REFERENCES
[2] Fine (M. E.), Greiner (E. S.) and Ellis (W. G.), J. Met., 1951, 3, 56.

DISCUSSION

M. Vogt. — Le Dr Lingelbach a mesuré la susceptibilité d'un chrome très pur préparé par l'Aeronautical Research Laboratory, Melbourne (Australia) et il a trouvé l'anomalie (figure 2 in Z. Physikal. Chem. (Frankfurt), 1958, 14, 11). Mais nous ne savons pas si c'est un point de Curie antiferromagnétique. L'objet principal de ce travail était la susceptibilité en fonction de la température des alliages dilués du Cr avec V, Mn, Fe, Co et Ni. Les résultats obtenus sont en concordance avec ceux de Mn de de Vries : la variation de la susceptibilité causée par V est petite, mais grande par Mn, Fe, Co et Ni. Il n'a pas été possible de trouver l'anomalie en fonction de la température, à cause de l'oxyde de chromie présent dans ces alliages, qui oblige à corriger les valeurs obtenues pour eux.

Mr. de Vries. — A measurement of the magnetic susceptibility of chromium obtained from Dr. Wain in the temperature range 10 °C-60 °C did not show a sharp change of slope at the temperature where the sample did have a rather sharp change of slope in the resistance temperature curve. (The relative accuracy in these measurements was about 0.04 %.)

Mr. Kurti. — It is very disturbing that apparently no specific heat anomaly has been observed in Cr in the neighbourhood of the Néel point, even if the actual jump at the Néel point were small, one should still expect an excess magnetic specific heat $C_m$ of such value that

\[ \int_{T_N}^{T} \frac{\Delta C_m}{T} \, dT \approx R \text{ cal}/\text{g} \cdot \text{atom}. \]

If the ordering is of a cooperative nature this magnetic entropy change should take place in a relatively narrow temperature range and therefore it should be possible to separate $\Delta C_m$ from the lattice and electronic specific heats.

Mr. de Vries. — As far as I know nobody has measured the specific heat in this region accurately enough to be sure whether the jump is there or not.

Mr. Wohlfarth. ← Dr. Kurti's difficulty may possibly be explained along the line of Lidiard's theory of the antiferromagnetism of metals.