the body-centered cubic and the face-centered cubic crystal. We obtain a distinct broadening of the curves in the corresponding amorphous cases. The broadening rises appreciably as the disorder increases. These results for the present simple theoretical model confirm the experimentally obtained exciton band broadening[2,3].

Acknowledgements. This work is part of a research program sponsored by I.R.S.I.A. (Brussels). One of us (W.C.) thanks this organisation for a grant. We wish also to thank Professor Dr. W. Dekeyser for his continuous interest and discussions.

REFERENCES

1) Christiaens, W. and Phariseau, P., Physica **46** (1970) 569.
2) Beaglehole, D., Phys. Rev. Letters **15** (1965) 551.
3) Moorjani, K., Bull. Amer. Phys. Soc. **13** (1968) 28.

Physica **47** (1970) 337–344 © *North-Holland Publishing Co.*

THE EFFECT OF PRESSURE ON THE NÉEL TEMPERATURE OF CHROMIUM-VANADIUM ALLOYS

W. DE DOOD, J. DE DOOD and P. F. DE CHATEL
Natuurkundig Laboratorium der Universiteit van Amsterdam, Nederland

Received 20 November 1969

Synopsis

The pressure dependence of the Néel temperature of chromium-vanadium alloys with less than 3 at % vanadium was determined by electrical resistivity measurements under hydrostatic pressure up to 3000 atm. The Néel temperature of each alloy varies linearly with pressure in the observed range, with a slope proportional to its value at $p = 0$ atm. The results are interpreted using a model due to Rice, Halperin, Barker and McWhan.

1. *Introduction*. The antiferromagnetism of chromium is known to persist upon the addition of small amounts of manganese and vanadium, and under high pressure. The influence of these factors on the antiferromagnetic structure is rather complex; without microscopic (*e.g.* neutron diffraction) measurements we can only roughly characterize it by the change of the Néel temperature (T_N).

It appears that the Néel temperature is very sensitive to the addition of small amounts of manganese and vanadium. From neutron diffraction experiments Hamaguchi *et al.*[1]) determined the magnetic structure of chromium and its alloys with manganese and vanadium. This investigation confirmed the existence of the spin density wave (SDW) state in chromium and revealed that the addition of manganese beyond a certain concentration ($\approx$ 2 at %) suppresses the SDW state in favour of a commensurate antiferromagnetic structure, and below this concentration the two phases coexist. In the alloys with vanadium the SDW state persists, although the Néel temperature falls rapidly with increasing vanadium concentration. The concentration dependence of the Néel temperature was established by the resistivity measurements of Trego and Mackintosh[2]). For vanadium concentrations below 3 at % and manganese concentrations below 0.75 at %, T_N was shown to depend exponentially on the average number of electrons per atom, n, thus:

$$T_N^{\text{alloy}} = T_N^{\text{Cr}} \exp[\alpha(n_{\text{alloy}} - n_{\text{Cr}})], \tag{1}$$

where α is the same constant for both alloy systems.

In retrospect, it is obvious that the early measurements of Bridgman[3]), in which he investigated the pressure dependence of an anomaly of unknown origin in the resistivity of chromium, point to the pressure sensitivity of its antiferromagnetism (which was unknown at the time of the measurements). The first systematic studies of the effect of pressure on the antiferromagnetic structure of chromium (as detected by neutron diffraction) were done by Litvin and Ponyatovskii[4]), and by Mitsui[5,6]). In a wider pressure range (up to 85 kbar), McWhan and Rice[7]) found that the Néel temperature is an exponential function of the pressure:

$$T_N^p = T_N^{p=0} \exp[\beta p], \tag{2}$$

where β is a constant. The value of β for chromium can be calculated from the formula given in terms of the relative volume change by McWhan and Rice[7]) and the bulk modulus $B_0 = 1620$ kbar quoted by them:

$$\beta = -16.5 \times 10^{-3}/1000 \text{ atm}.$$

In the experiments described in the present paper we measured the Néel temperature of alloys of different electron/atom ratio under pressure in order to decide whether it changes under the simultaneous variation of concentration and pressure in the way predictable from previous experiments. $(\mathrm{d}T_N/\mathrm{d}p)_{p\to 0}$ was measured as a function of the concentration for a number of Cr–V alloys containing less than 3 at % vanadium.

In the following section the preparation and chemical analysis of the samples and the experimental technique are described. The results of the measurements are summarized in section 3, and finally in section 4 the results are discussed in view of recent theoretical developments.

2. *Experimental procedure.* 2.1. Preparation and chemical analysis of the samples. Starting from Johnson and Matthey spectrographically standardized chromium and vanadium, Cr–V alloys containing less than 3 at % vanadium were prepared by arc-melting in an argon atmosphere. The obtained buttons were annealed at 1300°C for about one week, in vacuum-sealed silica tubes. After quenching and etching the buttons, specimens of approximate dimensions $10 \times 1 \times 1$ mm^3 were prepared by using a spark-cutting technique. The copper current and potential leads were spot welded to the samples.

With a wet chemical analysis the vanadium concentration was verified An atomic absorption spectrophotometer was used to detect some impurities. The following impurities were examined quantitatively:

$\mathrm{Mg} < 1$ ppm
Cu: 30 ppm
Fe: 40 ppm
$\mathrm{Al} < 30$ ppm
Mn: 20 ppm
Co: 80 ppm
Ni: 20 ppm

2.2. Measuring technique and apparatus. The high pressure equipment used for these measurements is similar to the one described by Franse[8]). In a copper-beryllium vessel helium gas was used as the pressure-transmitting medium; the pressures up to 3000 atm were detected by means of a Hottinger transducer. The uncertainty in the determination of the pressure was about 5 atm for all pressures, while the variation of the pressure during the measurements due to varying temperature was less than 10 atm.

For each sample a series of isobars was measured at temperatures in the range from 77 to 300 K. A copper-constantan thermocouple, which was mounted in a hole at the outside wall of the vessel, was used to determine the temperature. All points of an isobar were taken in thermal equilibrium, the uncertainty in the temperature was estimated to be less than 0.2 K.

The resistance has been measured by a four-probe dc technique; the current through the specimen was kept constant within 0.0001 %, while the voltage over the specimen was amplified by a Keithley millimicrovoltmeter, and determined with a Hewlett-Packard digital voltmeter. To eliminate thermopower effects the current was commutated.

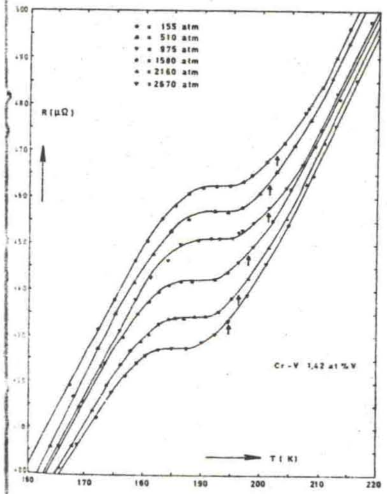

Fig. 1

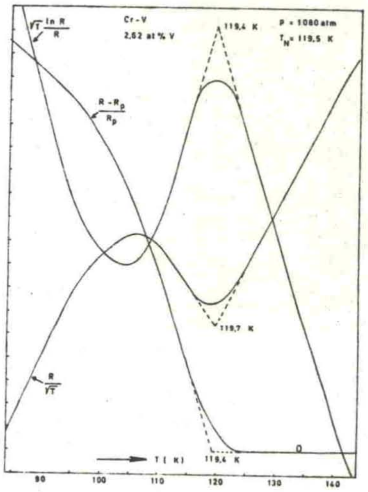

Fig. 2

Fig. 1. Electrical resistance *vs.* temperature for a Cr–1.42 at % V sample at different pressures. The arrows denote the determined Néel temperatures.

Fig. 2. Three graphical analyses in the region of the anomaly in the R *vs.* T curve for determination of T_N. The three extrapolations (dotted lines) give the same value for T_N (within the experimental error). R_p = extrapolated paramagnetic value for the resistance.

3. *Results*. Fig. 1 shows the resistance of a Cr–V sample as a function of the temperature in the range of pressures up to 2670 atm. In this alloy no minimum in the electrical resistivity versus temperature curve has been observed, in agreement with the experiments of Trego and Mackintosh[2]), and several other investigators[9,10,11]). To determine the Néel temperature from the resistivity versus temperature curves, we used three different graphical analyses: that of Trego and Mackintosh[2]) and two other analyses, displayed in fig. 2. As the character of the curves does not change with pressure, systematic errors in the determination of T_N do not play a role in calculating dT_N/dp. We determined dT_N/dp with the three analyses independently, the results agree with each other within the experimental error.

In fig. 3 the logarithm of the transition temperature is plotted against the vanadium concentration. We find a linear dependence, again in agreement with Trego and Mackintosh. The values for the Néel temperature represented here are slightly higher than expected from their measurements. This discrepancy may be explained by the fact that we used polycrystalline samples, in contrast with Trego and Mackintosh, who used single crystals for their measurements.

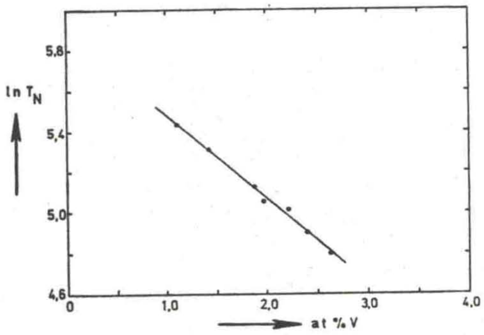

Fig. 3. ln T_N as a function of the concentration in Cr–V alloys.

In fig. 4 the pressure dependence of the Néel temperature is shown for the different alloys. The decrease of the Néel temperature is linear in pressure up to 3000 atm. For the initial slopes $(dT_N/dp)_{p\to 0}$ we took the slopes of these curves. In table I the results for all alloys are summarized. The values of T_N in this table, and those of $(dT_N/dp)_{p\to 0}$ are average values from the three analyses displayed in fig. 2.

The uncertainty in the Néel temperature itself is 0.4 K, while the uncertainty in $(dT_N/dp)_{p\to 0}$ is 0.3 K/1000 atm.

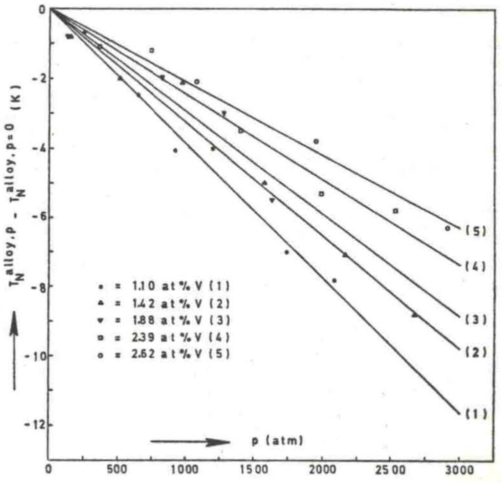

Fig. 4. Change of the Néel temperature *vs.* pressure for the different alloys.

TABLE I

Concentration (at %)	$T_N(p = 0)$ (K)	$(dT_N/dp)_{p\to 0}$ (K/1000 atm)
1.10	229.9	−3.86
1.42	203.4	−3.26
1.88	168.8	−2.95
1.96	156.8	not measured
2.21	151.3	not measured
2.39	135.0	−2.44
2.62	121.7	−2.09

4. *Discussion*. The outstanding feature of the antiferromagnetism of chromium and its dilute alloys with some of the transition metals is that the period of the magnetic structure is incommensurate with that of the crystal lattice. This structure was shown[12]) to arise from the condensation of bound electron-hole pairs, all having the same net wavevector $\mathbf{Q}$, which determines the period of the spin density wave (SDW) built up by them. The wavevector $\mathbf{Q}$ is uniquely determined by the geometry of the Fermi surface and thus does not need to coincide with any reciprocal lattice vector; hence the incommensurateness of the structure.

Fedders and Martin[13]) investigated the simplest two-band model displaying electron-hole pairing accompanied by SDW: two identical Fermi spheres, with wave vector difference Q, represent the electron and hole Fermi surfaces, and the Coulomb attraction between electrons and holes is described by a single parameter V. Mathematically the model is very similar to the BCS model for superconductivity, and so is the resulting expression for the transition (Néel) temperature, which reads:

$$k_B T_N = E_B \exp(-1/\lambda), \tag{3}$$

where E_B is of the order of the band width and $\lambda = VN(0)$, $N(0)$ being the density of states at the Fermi level.

From the experimental results mentioned in the introduction[2,7]) it is clear, that the effect of pressure and that of reducing the electron/atom ratio by alloying on the Néel temperature of Cr are very similar. In view of the result (3), this is not surprising: in fact α and β of eqs. (1) and (2) can be considered to be the first coefficients in a power-series expansion of $\lambda^{-1}(n, p)$.

Recently Rice *et al.*[14]) devised a model, based on an assumption regarding the joint density of states function, which predicts the concentration and pressure dependence of T_N, eqs. (1) and (2), correctly. The joint density of states, a function of two energy variables, x and y, is defined as:

$$N_Q(x, y) = \sum_{\boldsymbol{k}} \delta[x - \tfrac{1}{2}(\varepsilon_{\boldsymbol{k}}^{\mathrm{e}} - \varepsilon_{\boldsymbol{k}+Q}^{\mathrm{h}})]\, \delta[y - \tfrac{1}{2}(\varepsilon_{\boldsymbol{k}}^{\mathrm{e}} + \varepsilon_{\boldsymbol{k}+Q}^{\mathrm{h}})],$$

where $\varepsilon_{\boldsymbol{k}}^{\mathrm{e(h)}}$ is the single-particle energy in the electron (hole) band. If the two bands are identical, N_Q is almost independent of x and is proportional to $\delta(y)$. The model of Rice, Halperin, Barker and McWhan is defined by:

$$N_Q(x, y) = C_1\phi_1(y) + C_2\phi_2(y), \tag{4}$$

where $\phi_1(y)$ is sharply peaked at $y = 0$ and $\phi_2(y)$ has appreciable values only for $y > k_B T_N$. It has been shown[14]), that if C_1 and C_2 vary linearly with the electron/atom ratio and pressure, eqs. (1) and (2), respectively, are obtained from (4).

The experimental results quoted above [2,7]) can be considered to justify the model for N_Q, eq. (4). However, since the implications of the model regarding the band structure are not obvious, it is altogether not clear whether C_1 and C_2 are to be taken as constants plus linear combinations of n and p,

$$C = C_0 + C_n n + C_p p, \tag{5}$$

or: a "cross term" proportional to np is also allowed. In terms of the expansion of λ^{-1} (n, p) in (3), the question reduces of that of the importance of the term:

$$\frac{\partial^2(\lambda^{-1})}{\partial n \partial p} \Delta n p. \tag{6}$$

In the measurements of Trego and Mackintosh[2]) and McWhan and Rice[7]), the quadratic terms proportional to $\partial^2(\lambda^{-1})/\partial n^2$ and $\partial^2(\lambda^{-1})/\partial p^2$, respectively, were found to be negligible within the experimental error, but as in the experiments T_N was measured varying the electron concentration *or* the pressure, the importance of the cross term (6) cannot be ruled out by their evidence. It is only through the simultaneous variation of electron concentration *and* pressure that one can decide upon the importance of the term in eq. (6).

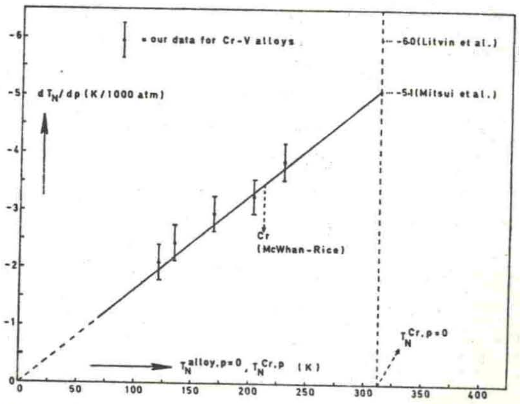

Fig. 5. dT_N/dp as a function of T_N (for Cr–V alloys in the limit $p \to 0$). The solid line represents the measurements of McWhan and Rice on pure chromium.

In fig. 5 we have plotted the slopes $(dT_N/dp)_{p\to0}$, given in table I, versus the transition temperature T_N. The linearity of $(dT_N/dp)_{p\to0}$ *vs.* T_N within the experimental error, together with the exponential dependence of T_N on concentration shown in fig. 3, proves that $(dT_N/dp)_{p\to0}$ varies exponentially with concentration. This is what one expects from previous measurements[2,7]): uniting (1) and (2) in the most straightforward way we have

$$T_N^{\mathrm{alloy},p} = T_N^{\mathrm{Cr},p=0} \exp[\alpha(n_{\mathrm{alloy}} - n_{\mathrm{Cr}}) + \beta p],$$

and hence

$$(dT_N^{\mathrm{alloy},p}/dp)_{p\to0} = \beta T_N^{\mathrm{Cr},p=0} \exp[\alpha(n_{\mathrm{alloy}} - n_{\mathrm{Cr}})] = \beta T_N^{\mathrm{alloy},p=0}.$$

Note that inserting a cross term of type (6) in the exponent, or, equivalently, allowing for the concentration dependence of β would contradict our experimental results. The slope of the straight line fitted to the points in fig. 5 gives thus β for all concentrations including pure Cr. The small scatter of our points around the line representing the results of McWhan and Rice[7]), displayed in fig. 5 shows that our value for β agrees within the experimental error with theirs. Our measurements give thus a full experimental justification of the model of Rice *et al.* in its form represented by eq. (5).

Acknowledgements. We wish to express our gratitude to Dr. J. J. M. Franse, Mr. H. C. Witteveld and Mr. W. Martijn for their help in designing and constructing the pressure vessel. We are very indebted to Drs. J. Kragten, Miss N. Punt and Mr. A. P. Reynaert for the chemical analysis, and to Prof. Dr. A. R. Miedema, Dr. C. J. Schinkel and Dr. F. R. de Boer for their critical reading of the manuscript.

This work was part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (Foundation for Fundamental Research on Matter) and was made possible by the financial support from the "Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek" (Netherlands Organisation for the Advancement of Pure Research).

REFERENCES

1) Hamaguchi, Y., Wollan, E. O. and Koehler, W. C., Phys. Rev. **138** (1965) A 737.
2) Trego, A. L. and Mackintosh, A. R., Phys. Rev. **166** (1968) 495;
Trego, A. L., thesis, Iowa State University (1965).
3) Bridgman, P. W., Proc. Amer. Acad. Arts and Sci. **68** (1932–1933) 27.
4) Litvin, D. F. and Ponyatovskii, E. G., Soviet Physics – Doklady **9** (1964) 388.
5) Mitsui, T., Physics of solids under high pressure (Proc. of the first Int. Conf. on the Physics of solids at high pressures, Tucson Arizona (1965) p. 213.
6) Mitsui, T. and Tomizuka, C. T., Phys. Rev. **137** (1965) A 564.
7) McWhan, D. B. and Rice, T. M., Phys. Rev. Letters **19** (1967) 846.
8) Franse, J. J. M., thesis, Universiteit van Amsterdam (1969).
9) Vries, G. de, J. Phys. Radium **20** (1959), 438.
10) Komura, S., Hamaguchi, Y. and Kunitomi, N., J. Phys. Soc. Japan **23** (1967) 171.
11) Arajs, S., Canad. J. Phys. **47** (1969) 1005.
12) Overhauser, A. W., Phys. Rev. **128** (1962) 1437; J. appl. Phys. Suppl. **34** (1963) 1019; Lomer, W. M., Proc. Phys. Soc. **80** (1962) 489.
13) Fedders, P. A. and Martin, P. C., Phys. Rev. **143** (1966) 245.
14) Rice, T. M., Barker jr., A. S., Halperin, B. I. and McWhan, D. B., J. appl. Phys. **40** (1969) 1337;
Rice, T. M., Halperin, B. I. and McWhan, D. B., Proc. of the XI-th Intern. Conf. on Low Temperature Phys. (St. Andrews, 1968), 1308.

Physica 47 (1970) 345–372 © *North-Holland Publishing Co.*

A RIGOROUS APPROACH TO A MARKOFFIAN MASTER EQUATION

L. LANZ
Istituto di Fisica del'Università, Milano and Istituto Nazionale di Fisica Nucleare, Sezione di Milano, Italia

L. A. LUGIATO
Istituto di Fisica dell'Università, Milano, Italia

Received 28 July 1969

Synopsis

The part $\Phi_0(t)$ of the statistical operator (or density function) which is relevant for the description of macroscopic dynamics is treated. The few mathematical properties of the solution of Zwanzig's generalized master equation which are important for the deduction of a markoffian master equation for $\Phi_0(t)$ are pointed out. On the basis of such results the conditions under which markoffian macroscopic dynamics exists are discussed. A comparison with the results of I. Prigogine's school is finally made.

1. *Introduction.* In a previous paper[1] we discussed the problem of the approach to equilibrium for the macro-observables of an insulated macroscopic system.

The limit for $t \to +\infty$ of the solution of a generalized master equation (G.M.E.) was proved to be given by the microcanonical ensemble; for this result only very general mathematical properties of the Laplace-transformed nucleus of the G.M.E. are relevant. One expects that this approach to equilibrium is well described, at a macroscopic level, by a markoffian master equation; this is a much more difficult problem to study, since it requires a more detailed analysis of the dynamics of macro-observables.

In this paper we elaborate on some peculiar mathematical features of the G.M.E. which make it possible for a macroscopic markoffian evolution to exist. The main tool for this analysis is a systematic use of the spectral representation of the relevant operators in a finite-dimensional Liouville-space.

The mathematical results, obtained in sections 2 and 3, are discussed in a less rigorous way in section 4 and some physical consequences are obtained. The main conclusion is that a markoffian behaviour exists if a suitably defined characteristic time τ_0 is microscopic with respect to the time scale