

NEUTRON DIFFRACTION AND SCATTERING STUDIES AT J. A. E. R. I.

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Résumé. — Les études de diffraction neutronique et diffusion exécutés au J. A. E. R. I. en 1962 sont brièvement décrites ici :

1) *Pouvoir réflecteur des neutrons collimatés par un cristal mosaïque* : Un calcul semblable à celui de la théorie de Bacon et Lowde tenant compte des extinctions secondaires a été effectué comprenant l'effet de la collimation des neutrons. Les résultats théoriques impliquent que le pouvoir réflecteur décroît lorsque la collimation croît. Ces résultats sont comparés avec l'expérience.

2) *Structure cristalline de UF_4* : Dans le cadre de recherches sur les actinides, la position du fluor a été déterminée au moyen de techniques de poudres. Les raies de diffraction aux rayons X et le modèle le plus plausible est déterminé par comparaison des intensités observées et théoriques, ces dernières étant déduites d'un modèle cristallo-chimiquement stable. La distance fluor-uranium, déduite de l'analyse radiale de Fourier, est en accord avec le modèle.

3) *Diffusion de neutrons par les hydrides* : La transmission des neutrons à travers TiH_{2-x} a été étudiée en fonction de la concentration en hydrogène et de la température. Bien que la température de l'expérience dépasse le point de transformation cubique-quadratique, aucun changement notable n'a été observé indiquant la constance de la fréquence d'Einstein de la branche optique au long des expériences.

4) *Structure Magnétique de Mn-Cr*. Des mesures de résistivités électrique, de susceptibilité magnétique et des études de diffraction neutronique ont été faites sur des alliages Mn-Cr. Les résultats montrent que ces alliages sont antiferromagnétiques et suggèrent que les propriétés magnétiques sont à interpréter en termes de la théorie des bandes.

Abstract. — The neutron diffraction and scattering studies performed at JAERI from 1962 to 1963 are briefly described.

1) *Reflectivity of the collimated neutrons from a mosaic crystal* : A calculation similar to Bacon and Lowde's theory, taking secondary extinction into account, has been carried out including the effect of neutron collimation. The theoretical results imply that the reflectivity decreases with increasing collimation. These results are compared with experiment.

2) *Crystal structure of UF_4* : In a series of investigations on actinide elements, the positions of fluorine have been determined by means of powder diffraction techniques. The diffraction lines are compared with the X-ray diffraction pattern and the most plausible model is determined by comparing the experimental intensity with the theoretical one deduced from geometrical considerations. The uranium — fluorine distance derived from a radial Fourier analysis is proved to be consistent with the model.

3) *Scattering of neutrons from hydrides* : The transmissivity of neutrons through TiH_{2-x} has been investigated as a function of hydrogen concentration and temperature. Although the experimental temperature exceeds the cubic-tetragonal transformation temperature, no remarkable change has been observed indicating the constancy of the Einstein frequency of the optical branch throughout the experimental temperature range.

4) *Magnetic structure of Mn-Cr*: Electrical resistivity and magnetic susceptibility measurements and neutron diffraction studies have been made on Mn-Cr alloys. The results show that these alloys are antiferromagnetic and suggest the magnetic properties of these alloys to be interpreted in terms of band theory.

I. Introduction. — In the early stage the activities of our neutron diffraction group in JAERI were concentrated mainly on instrumental developments and studies on uranium compounds. The first two parts of the present paper deal with them. Since the high power reactor JRR-2 was not available for routine operation until 1962, a neutron transmission experiment using a small training reactor JRR-1 was started and yielded some conclusions on the lattice dynamics of hydrides as given in the third part of this paper. The studies on magnetic materials have been started since early spring 1963 and the antiferromagnetism of Mn-Cr alloys has been investigated in this period as well as the structure of Mn Te which is presented in this conference as an independent paper.

The principal facilities used in the present investigations are a powder specimen type neutron diffractometer [1] installed at JRR-2 (10 MW, CP-5 Type Reactor) and a small monochromator at JRR-1 (50 kW, Water Boiler Type Reactor).

II. Reflectivity of collimated neutrons by a mosaic single crystal. — In designing a neutron diffractometer, it is necessary to know the reflectivity of neutrons by a monochromating single crystal. Bacon and Lowde have previously developed a method to calculate it taking the secondary extinction and the true absorption into account [2]. According to their results the reflectivity should increase monotonically with increasing mosaic spread since the crystal imperfectness reduces the secondary extinction effect. This leads to the unreasonable consequence that the most imperfect crystal such as a powder specimen should have the highest reflectivity. Since their calculation integrates all the neutrons scattered in every direction, the reflectivity diverges for the infinitely imperfect crystals. Therefore, it is aimed in the present investigation to improve their theory by setting up an appropriate restriction to the direction of the scattered neutrons after passing collimators.

Assuming the restriction effect of a collimator on neutrons as Gaussian with respect to the incident direction [3], the reflectivity in the general form is represented by :

$$R(\alpha_1, \alpha_2, \eta, Q/\mu, t_0) = \eta \int_{-\infty}^{\infty} A \exp\left(-\frac{1}{2} Bx^2\right) \int_{\left[\frac{1}{2}(D+1) + D^{1/2} \coth(CD)^{1/2}\right]} dx, \quad (1)$$

with the following abbreviations :

$$A = Q/\mu\eta, \quad B = 1 + 2\eta^2 (\alpha_1^{-2} + \alpha_2^{-2}), \quad (1')$$

$$C = \mu t_0 / \sin \Theta, \quad D = 1 + 2A \exp\left(-\frac{1}{2} x^2\right),$$

where the notations are as follows :

α_1 and α_2 : angular divergences of the first and second collimators, respectively.

η : angular spread of mosaic blocks.

Q : crystallographic quantity.

μ : true absorption coefficient.

t_0 : crystal thickness.

Θ : Bragg angle.

Since the equation contains many independent variables, an assumption is introduced for simplification, that is, the effect of the collimation does not depend on the thickness of the crystal. This assumption is expressed functionally as :

$$\frac{R(A, B, C)}{R(A, B, \infty)} = \frac{R(A, 1, C)}{R(A, 1, \infty)}. \quad (2)$$

Here $R(A, 1, C)$ is the reflectivity for the extreme case of infinite angular divergence of the collimator already calculated by Bacon and Lowde. $R(A, B, \infty)$ is obtained from eq. (1) as

$$R(A, B, \infty) = \eta \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} Bx^2\right) \int_{\left[\frac{1}{2}(D+1) + D^{1/2}\right]} dx. \quad (3)$$

The extreme value $R(A, 1, \infty)$ is obtained from (3) by inserting $B = 1$. Therefore the general value of the reflectivity $R(A, B, C)$ is calculated by combining these values for reflectivities by using eq. (1).

A typical value for the reflectivity obtained by numerical calculation is shown in figure 1 for Pb (200) as a function of the mosaic spread where the crystal thickness is assumed to be 10 mm and the angular divergences of the first and the second collimators are assumed to be the same. It is apparent from this figure that the reflectivity should have a maximum for an optimum degree of mosaic spread and different values for neutrons with different angular divergences. The first conclusion drawn here indicates the importance of the selection of the optimum mosaic spread [4].

The second conclusion that the theoretically calculated ratio of $R(30')/R(15')$ is 1.96 has been confirmed experimentally by using collimators with angular divergences of 30' and 15'. After correcting the geometrical decrease of neutrons in passing through the collimator, the experi-

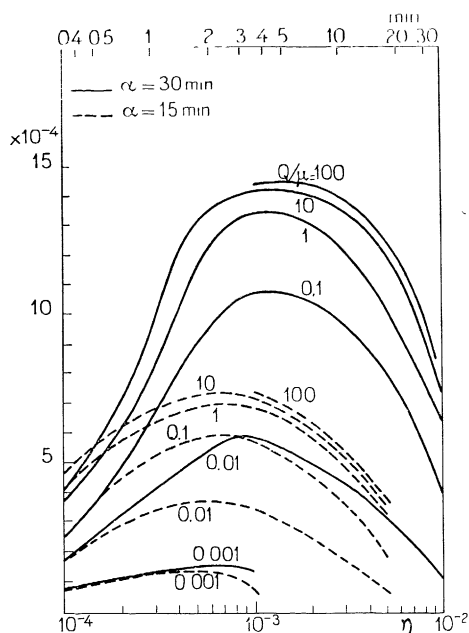


FIG. 1. — Reflectivity of the collimated neutrons as a function of the mosaic spread.

mentally obtained ratio of $R(30')/R(15')$ is 1.60 while the theoretical one is 1.96 and that obtained from Bacon and Lowde's formula is 1.00. Considering the geometrical misfit which is inherent to the collimator especially for the finer one, the agreement between theoretical and the experimental values seems to be satisfactory.

Caglioti and his coworkers have calculated the luminosity and the resolution of the neutron diffractometer by tracing the path of individual neutron rays [5], [6], [7]. In contrast to the Bacon and Lowde theory they have included the effect of collimation, but have neglected secondary extinction assuming that the intensities of reflected neutrons are proportional to the volume of the crystal. Furthermore they have assumed the distribution of the mosaic blocks in the monochromating crystal as Gaussian which is normalized to unity at the peak of the Gaussian distribution. However, if the distribution of the mosaic blocks is normalized by the integrated area as by Bacon and Lowde

$$W(\Delta) = \frac{1}{\sqrt{2\pi}\eta} \exp(-\Delta^2/2\eta^2),$$

the calculation developed by Caglioti should lead to the luminosity L as

$$L = \alpha_1, \alpha_2, \alpha_3 / (\alpha_1^2 + \alpha_2^2 + 8\eta^2)^{1/2},$$

in which $\alpha_1, \alpha_2, \alpha_3$ are the angular divergences of the first, second and third collimators, respectively. The luminosity thus obtained should decrease with the angular spread of the mosaic blocks.

The present result shows that the actual behavior of the reflectivity is a compromise of Bacon and Lowde's and Caglioti's theories. If the mosaic spread is small the reflectivity increases with it because of the increasing angular range of the reflection. However, if the mosaic spread is large enough, the reflectivity should decrease with it, due to the collimation effect.

The reflectivities of several different crystals have been calculated by using the present results and the choice of monochromating crystals for various experimental purposes is recommended in another paper which will be published in *Journal of the Physical Society of Japan*.

III. Neutron and X-Ray studies on uranium tetrafluoride. — Zachariassen [8] has observed that the uranium tetrafluoride is isostructural with zirconium tetrafluoride and has deduced the positions of uranium atoms; Burbanks and Bensey [9] have recently studied a single crystal of zirconium tetrafluoride and have determined the positions of zirconium and fluorine atoms. In the present investigation powder samples of UF_4 have been studied by means of X-Rays and neutron diffraction. Whereas the X-Rays analysis is insensitive to the positions of fluorine atoms in UF_4 , the reflections of neutrons by fluorine atoms in UF_4 can be observed with sufficient intensity since the scattering amplitudes are not too much different ($U: 0.85 \times 10^{-2}$ cm, $F: 0.55 \times 10^{-12}$ cm) [10].

The samples were refined by Atomic Fuel Corporation Japan with impurities of H_2O less than 0.10 %, UO_2 0.3 % and UO_2F_2 0.02 %. The reflected intensities of X-Rays were measured by G. M. counter method with $CuK\alpha$ radiation mono-

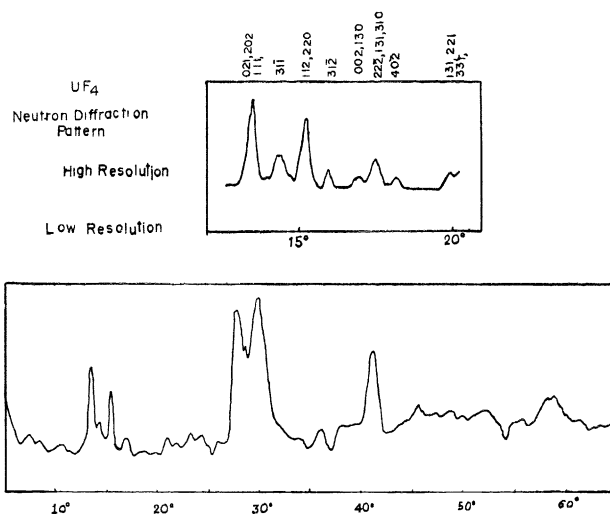


FIG. 2. — Neutron diffraction patterns for UF_4 . The high resolution pattern is taken for the structure factor calculation and the low resolution pattern for the Fourier analysis.

chromatized by a curved crystal of LiF. The X-Rays patterns were analyzed by using Zachariasen's U-coordinates with the unit cell dimensions

$$a = 12,79 \text{ \AA}, \quad b = 10,72 \text{ \AA}, \quad c = 8,39 \text{ \AA},$$

$$\beta = 126^\circ 10', \quad C_{2h}^2 - C 2/c.$$

The neutron diffraction pattern shown in figure 2 has been taken with a wavelength of 1,00 Å and was analysed by assigning F-positions by trial and error. Since the nearest U-U distance is approximately equal to the sum of the diameters of U^{4+} and F^- , the F atoms were first placed at the midpoint of the nearest U-U pairs. After several modifications of the fluorine positions so as to obtain the best fit between the experimental and the calculated intensities, as shown in figure 3, the atomic positions shown in figure 4 were finally determined. The structure is seen to be constituted by distorted UF_4 polyhedra in which the

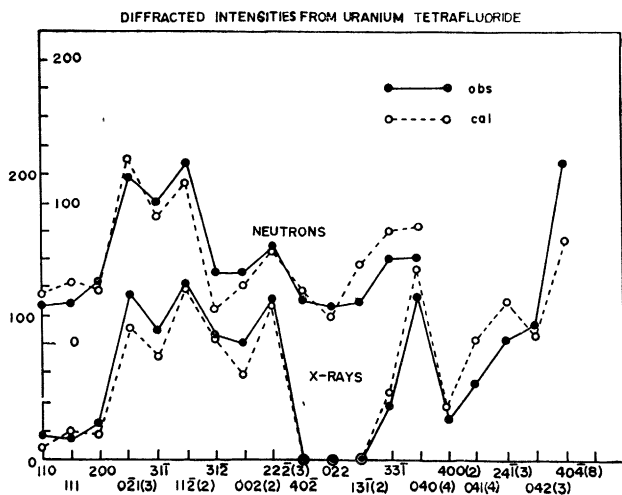


FIG. 3. — The comparison between the calculated and the observed intensities of X-ray and neutron reflections by UF_4 .

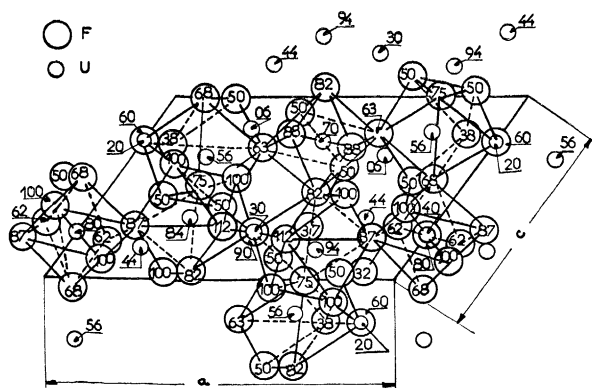


FIG. 4. — Crystal structure of UF_4 .

corner atoms are shared by two neighboring polyhedra.

In order to confirm the present conclusion which is obtained from a relatively small number of observed reflections, the radial distribution functions were calculated in a way similar to that used for an amorphous solid or liquid. After correcting for background level, sample holder reflections, Compton scattering, polarization factor and the appropriate factors, the X-Rays and the neutron patterns have been subjected to a radial Fourier analysis up to the scattering angle of

$$2 \sin \Theta / \lambda = 0,80.$$

The X-Rays radial distribution curve shows a diffuse peak at about 4,8 Å with an integrated area of $6,0 \pm 0,6 \times 10^{-5}$ electronic units. The position and the integrated areas of the peak are very close to the values for the nearest U-U pairs, which are about 4,6 to 4,8 Å and $6,8 \times 10^{-5}$ electronic units respectively according to the present model. Two peaks are observed in the neutron radial distribution function at 2,5 Å and 4,6 Å. The former corresponds to the U-F and F-F distances and the latter to the U-U, U-F and F-F distances. The integrated areas for the two peaks are 90 ± 20 barns and 300 ± 20 barns, which are compared respectively with 100 barns and 300 barns calculated from the present model.

The fairly good agreement of the measured radial distribution functions with the calculated ones seems to support the atomic structure model proposed here from the powder diffraction patterns of UF_4 . Finally, it should be noted that this structure is quite similar to the structure of ZrF_4 determined by Burbank and Bensey [9],

IV. Measurement of the optical vibrations in titanium hydride. — According to Fermi's theory [11], the thermal neutron cross section of hydrides shows a minimum at the energy level of the optical vibration [12]. This provides a method of investigation of lattice vibrations in hydrides. X-Ray [13] and neutron diffraction [14] studies have shown that the titanium hydride transforms from tetragonal to cubic at about 310 °K. Above this temperature, the stoichiometric compound TiH_2 crystallizes in the fluorite structure. For the compound with hydrogen less than stoichiometry, the tetrahedral hydrogen positions become randomly vacant. Very recently Geshi and Takagi [15] have investigated the phase transformation mechanism. The purpose of the present investigation is to determine the influence of the phase transformation and hydrogen concentration on the cohesive energy of TiH_2 by means of the measurement of the energy level of the optical vibration.

The samples were prepared from metallic powder

of titanium and purified hydrogen. In order to remove the contained gas, the titanium powders were preheated in vacuum for several hours, and then annealed at 600 °C for 4 hours sealed with the known amount of the hydrogen gas. The final amount of hydrogen was checked by the difference of the sample weight before and after the heat treatment.

The neutron transmission cross section has been measured by a monochromator at JRR-1. The monochromating crystal used was lead (200) and the neutrons were collimated by Soller slits with an angular divergence of 15 minutes. The samples were set in the cryostat cooled by dry ice or heated by an electric heater wound around the samples. The total cross sections have been measured for $\text{TiH}_{1.3}$; $\text{TiH}_{1.6}$ and TiH_2 at room temperature and those for TiH_2 have again been measured at -79°C , $+20^\circ\text{C}$ and $+60^\circ\text{C}$ as shown in figure 5.

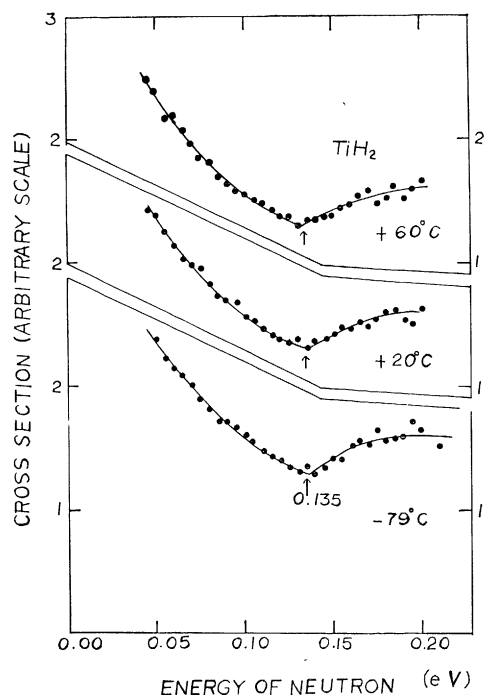


FIG. 5. — Thermal neutron cross section for TiH_2 at various temperatures.

All experimental curves including concentration and temperature dependences have shown similar behaviours and provide the same Einstein frequency of 0.135 ± 0.007 eV.

The present results also support the theoretical conclusion by Lehman, Wolfram and De Wames [16] that the optical level of ZrH_2 which is quite similar to TiH_2 is expressed by a nearly single Einstein frequency but contradict the experimental result of hydrogen diffusion in TiH_x that the frequency factor should increase with the

hydrogen concentration [17]. This contradiction may imply that the jump of a diffusing atom is not directly related to the optical vibration but is influenced by the environment in a complex manner.

The full paper and the detailed discussion will appear in *Journal of the Physical Society of Japan*. Similar studies for other hydrides such as VH_2 are now in progress.

V. Magnetic structure of Mn-Cr alloys. —

Unusual properties of chromium in the $3d$ transition metals have been studied by means of neutron diffraction [18], [19], but the origin of these properties has not been clear until now. The purpose of the present work is to add informations on the properties of chromium by studying Cr alloys containing Mn. Kasper and Waterstrat [20] have found antiferromagnetic reflections in the neutron diffraction patterns of CrMn alloy, but no other properties have been found which prove the existence of antiferromagnetism in these alloys. The chromium side alloys of the Mn-Cr system have been studied in detail in the present experiment.

The samples were prepared from 99.99 % chromium and manganese, melted by arc furnace in

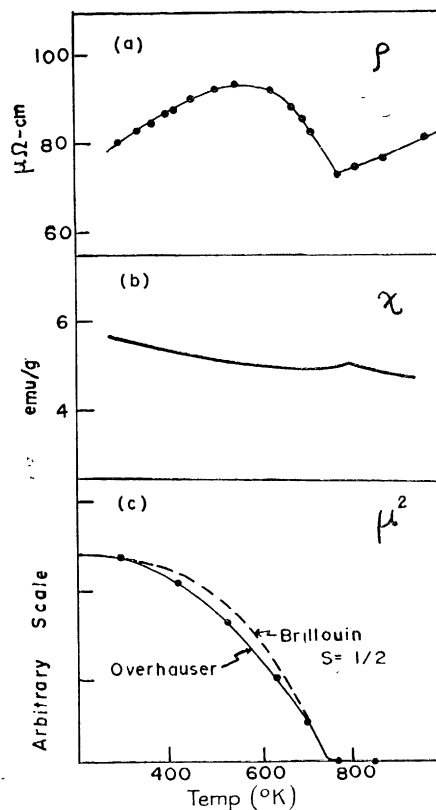


FIG. 6. — Temperature dependences of the electrical resistivity, magnetic susceptibility, and magnetic moment of $\text{Mn}_{30}\text{Cr}_{70}$.

the atmosphere of argon gas. For the homogenization the samples were sealed in evacuated quartz tubes and annealed at 1 050 °C for one week. Figure 6 shows the temperature dependence of the electrical resistivity, magnetic suscep-

tibility and magnetic moment of the alloy with 30 atomic percent manganese. The magnetic moment was calculated from the difference pattern shown in figure 7 which is obtained by subtracting the pattern taken at 600 °C from that taken at

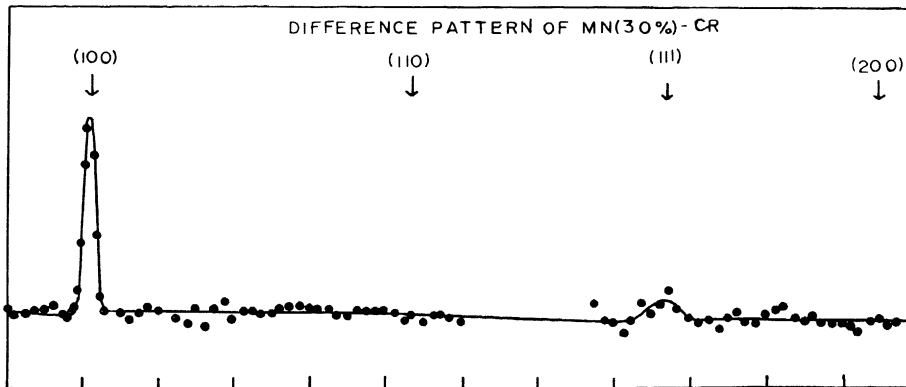


FIG. 7. — Difference pattern of $Mn_{30}Cr_{70}$ obtained by subtracting the neutron diffraction pattern for 600 °C from that for room temperature.

room temperature. The quantitative comparison has proved that the spin arrangement of this alloy is a simple antiferromagnetic structure represented as $[(000), - (000)]$ in the Gersch-Koehler's notation [24]. (The measurement at various temperatures has been made by setting samples in a furnace with a thin wall so that small bumps were observed in the original diffraction patterns but these vanish in the difference pattern as shown in the figure.) Fine structure has not been detected in the magnetic peak suggesting that the magnetic structure may not be modified by the long range structure. The theoretical curve of the temperature dependence of the magnetic moment is shown in figure 6(c) with the experimental value. It should be noted that the experimental value shows the best fit with the band theoretical values obtained by Overhauser [22]. The magnetic susceptibility was measured accurately by the automatic magnetic balance and the small maximum shown here has appeared reproducibly in several experimental runs including heating and cooling processes. The electrical resistivity which has been reported as a good indication of antiferromagnetic ordering in chromium [23] also shows an anomaly at the same temperature. It is concluded from these three experiments that Mn-Cr with 30 atomic percent manganese has an antiferromagnetic structure below 770 °K.

Concentration dependences of the magnetic moment and the Néel temperature are shown in figure 8. The Néel temperature is determined by the measurement of the electrical resistivity and the magnetic moment by neutron diffraction. The magnetic moment for the alloy with 48 percent

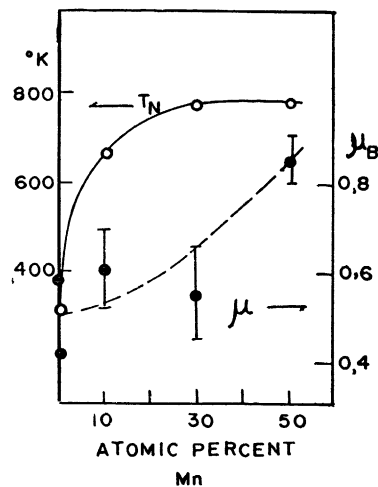


FIG. 8. — Concentration dependence of the Néel temperature and the magnetic moment for the Mn-Cr system.

manganese is cited from the work by Kasper and Waterstrat [20].

Although the properties of the pure chromium and the electrical resistivity shown above are interpreted in terms of the band picture [22], [23], a theoretical investigation is expected to be carried out to explain the various properties of chromium and chromium alloys in a unified scheme.

VI. Conclusion. — The neutron diffraction studies of JAERI now in progress are mainly concerned with magnetic materials including compounds and metallic alloys. Specimens with NiAs

type structure such as VS, VSe, VTe and others are in preparation, and single crystals of these samples as well as MnTe will be prepared too. Several alloy specimens such as Mn-Cr and face-centered cubic antiferromagnetics such as Fe-Mn and Au-Cr have been prepared for the magnetic structure determination.

Studies on the scattering of cold neutrons by lattice imperfection are also scheduled in which

several precipitation alloys will be used. The studies of hydrides are further continued on V-H, Ta-H and Nb-H.

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