Solid State Communications, Vol. 23, pp. 859–862, 1977. Pergamon Press. Printed in Great Britain

HELICAL MAGNETIC STRUCTURE IN CrB_2

S. Funahashi and Y. Hamaguchi

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, 319-11, Japan

and

T. Tanaka and E. Bannai

National Institute for Researches in Inorganic Materials, Sakura-mura, Ibaraki-ken 300–31, Japan

(*Received* 22 *May* 1977 *by T. Nagamiya*)

A cycloidal magnetic structure was discovered in CrB_2 by neutron diffraction using a thin single crystal plate prepared with natural boron. The propagation vector was determined to be $\tau = 0.285\,\tau_{110}$. The magnetic moments of a magnitude of $0.5 \pm 0.1\mu_B$ turn in the a–c plane.

BARNES AND CREEL [1] found in 1969 that the NMR signal of ^{11}B in CrB_2 disappears at 88 K. They proposed a chromium-like magnetism for CrB_2 because the resonance behavior near that temperature resembled strongly that of ^{53}Cr in pure chromium and of ^{51}V in Cr–V alloy near T_N. Castaing *et al.* [2] showed by magnetic measurements of $V_{1-x}Cr_xB_2$ compounds that the magnetic ordering occurs for compositions of x larger than 0.77 and that T_N of CrB_2 is 86 K. These results suggest itinerant antiferromagnetism in these materials.

Since the thermal neutron absorption cross section of natural boron is very large ($\sigma = 430 \times 10^{-24}$ cm^2 for $\lambda = 1.08$ Å neutron), it is not easy to measure magnetic neutron diffraction by polycrystalline borides, unless the magnetic moment is large. Castaing [3] measured neutron diffraction by polycrystalline CrB_2 enriched with ^{11}B. He observed three very weak supplementary diffraction lines presumably of magnetic origin at low temperatures. These lines, however, could not be identified definitely.

Liu *et al.* [4] calculated the energy bands of CrB_2 by using the KKR method in the muffin-tin potential approximation. They proposed a spin density wave (SDW) along the c-axis due to the nesting of the seventh band Fermi surface, and they calculated the generalized susceptibility $\chi(Q)$ in that direction. It was shown that $\chi(Q)$ had a maximum between the Γ-point and the A-point. One of the three magnetic lines observed by Castaing could be explained by this model, but others could not be identified.

Recently, Tanaka *et al.* [5] succeeded in growing large single crystals of CrB_2 by the floating zone method in a pressurized atmosphere. They measured the electrical resistivity, the Hall coefficient and the magnetic susceptibility of the single crystals [6], and confirmed that the magnetic ordering occurs at 88 K. The ordering temperature decreases slightly with nonstoichiometric deficiency of boron content.

We have carried out neutron diffraction measurements by using the single crystal, and determined the magnetic structure. Though the neutron absorption by natural boron is very strong, the material is still tractable when compared with gadolinium for example.

The single crystal of CrB_2 grown by the method described in reference [5] was cut into a rectangular plate of an area about 7×30 mm^2. The plate was polished to become as thin as 0.23 mm, in order to gain sufficient diffracted neutron intensity of various reflections in the transmission configuration. The plate surface was parallel to the crystalline hexagonal plane. The triple-axis neutron spectrometer installed in JRR-2 reactor was used to measure the diffraction.

Figure 1 shows the θ–2θ diffraction pattern scanned along the reciprocal $[110]^*$-axis at a low temperature. The measurement was carried out with 1.0 Å wavelength neutron, and the Ge (111) analyzer was used to eliminate the $\lambda/2$ contamination coming from the pyrolytic graphite monochromator. Two magnetic satellite reflections are seen at 2θ angles of 11.2° and 28.25°. Two weak extra lines indexed as 1/3, 1/3, 0 and 2/3, 2/3, 0 are not of magnetic origin because their intensity does not change even at room temperature. The peaks at 24.9° and 29.0° are the 111 and 200 reflections, respectively, of aluminium of the sample holder. The intensity of the fundamental reflections does not change with temperature, while the satellites disappear at high temperatures. The satellite positions are explained by an incommensurate magnetic structure defined by a propagation vector $\tau = 0.285\tau_{110}$. Here τ_{110} is the reciprocal lattice vector of 110, i.e. $|\tau_{110}| = 2\pi/(a/2)$.

Figure 2 shows the satellite reflection points in the

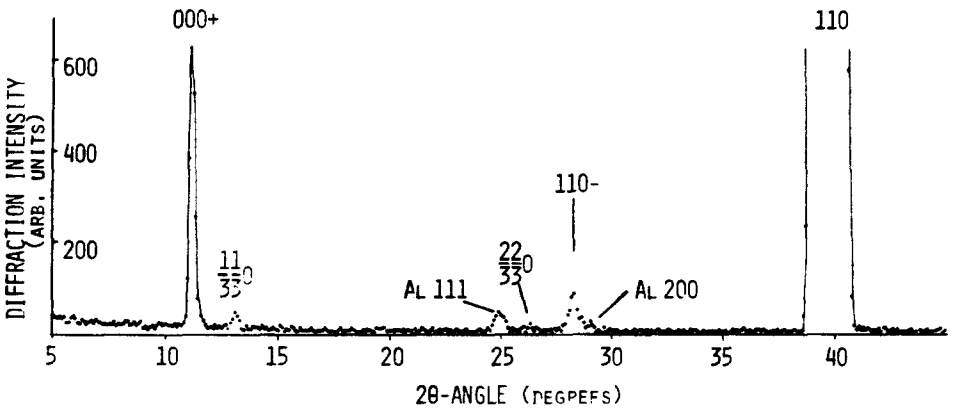

Fig. 1. Profile of $\theta-2\theta$ scanning along the $[110]^*$ axis at about 14 K. Reflections at 1/3, 1/3, 0 and 2/3, 2/3, 0 do not change up to the room temperature.

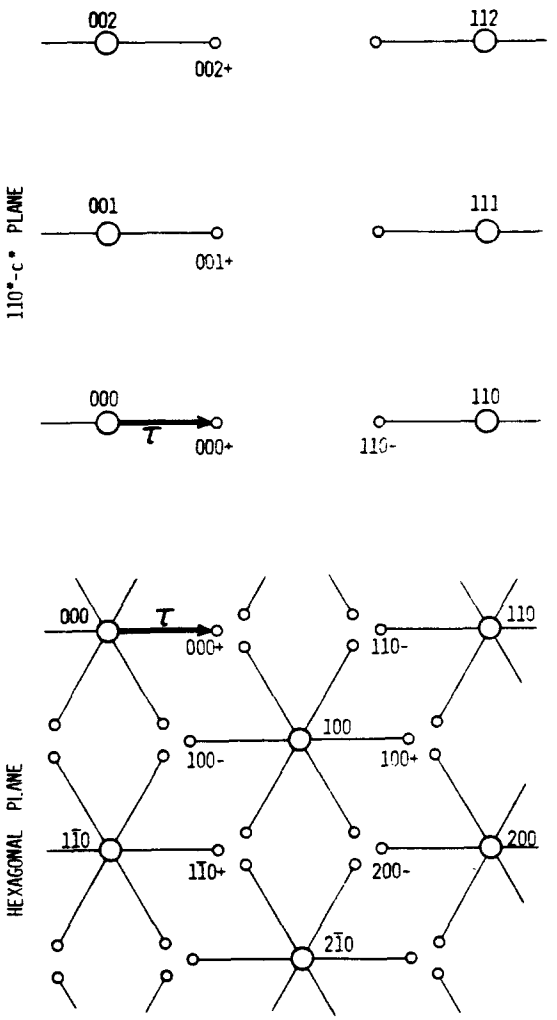

Fig. 2. Schematic picture of satellite diffraction positions in the reciprocal lattice planes. The upper figure represents the plane defined by $[110]^*$ and c^*. The lower is the hexagonal plane.

reciprocal lattice plane perpendicular to the c^*-axis as well as in the plane including the $[110]^*$-axis and the c^*-axis. Two satellite lines in Fig. 1 correspond to points indexed as 000+ and 110— in Fig. 2. Many satellite reflections corresponding to crystallographically equivalent propagation vectors, i.e. $\tau = 0.285\tau_{110}$, $0.285\tau_{2\bar{1}0}$ and $0.285\tau_{\bar{1}20}$, were observed.

In order to determine the magnetic structure, the intensity of those satellite reflections which are generated by a single propagation vector was measured with the $\theta-2\theta$ scanning in the two reciprocal planes described above. The diffracted neutrons were counted directly without the analyzer in these scannings, because there was no possibility of the $\lambda/2$ contamination in the incommensurate satellite reflections. The wavelength was chosen to be 2 Å to obtain good resolution.

The observed intensity was corrected by taking into account the Lorentz factor, the absorption and the magnetic form factor. The corrected intensity is proportional to the magnetic structure factor. It is plotted in Fig. 3 as a function of κ^2_{110}. Here κ_{110} is the direction cosine of the scattering vector with respect to the reciprocal $[110]^*$ direction. The absorption cross section of boron was assumed to be $\sigma = 796 \times 10^{-24}$ cm^2 for $\lambda = 2$ Å. The form factor of pure chromium reported by Stassis *et al.* [7] was used. A considerable scatter of the corrected intensity in Fig. 3 is due to the large absorption correction which changes greatly from satellite to satellite.

The square root of the 001+ satellite intensity is plotted in Fig. 4 as a function of temperature, together with the calculated magnetization in the molecular field approximation with $S = 1/2$. The satellite disappears at about 84 K. Little change of the satellite position was observed up to T_N.

Since no bulk magnetization has been observed, it is not necessary to consider a conical magnetic structure which gives rise to a ferro or a ferrimagnetic moment.

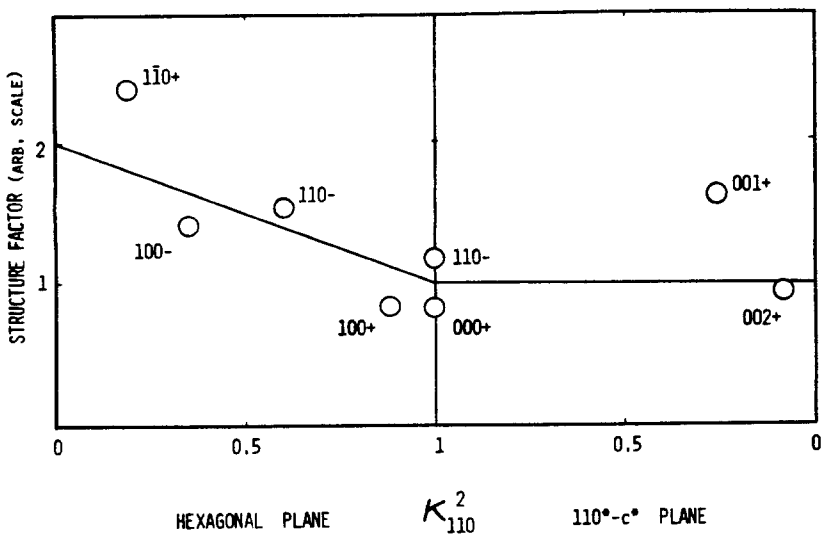

Fig. 3. Corrected intensity as a function of κ^2_{110}. The left half of the figure represents the satellite intensity in the hexagonal plane, while the right half is for the $[110]^*$-c^* plane. The solid line represents the calculated structure factor of a cycloid such that the spins turn in the a–c plane with a moment of $0.5\mu_B$.

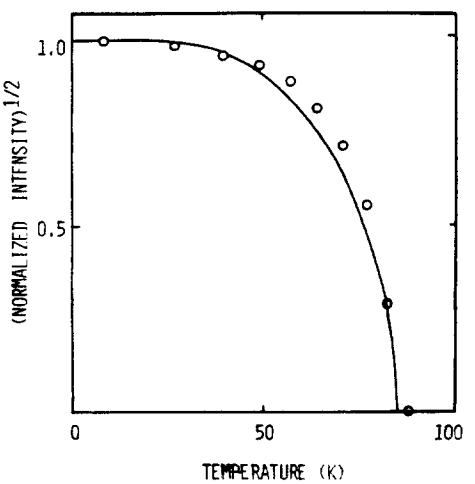

Fig. 4. Square root of the 001+ satellite intensity as a function of temperature.

Two-sublattice conical structure in which the axial components give rise to antiferromagnetic structure is discarded, because any half-integer superlattice reflections were not detected on the principal axes.

In consequence, we examine the single sublattice structure. The simplest incommensurate structure is a sinusoidal SDW. But it fails certainly to explain the experimental results, because there is no indication in Fig. 3 that the structure factor vanishes either at $\kappa^2_{110} = 1$ or at $\kappa^2_{110} = 0$, even if we consider the experimental accuracy. It is expected for the SDW model that the magnetic diffraction vanishes when the scattering vector is turned to become parallel to the easy direction of magnetization.

The next simple structure is a helical one. It is composed of two kinds of SDW in a proper phase. The helical structure is classified into the proper screw and the cycloidal one. It is found that the cycloidal structure in which magnetic moments turn in the $[110]^*$-c^* plane explains the overall feature of the experimental results shown in Fig. 3. The magnitude of the magnetic moment is determined by comparing the satellite intensity with the nuclear Bragg intensity. It is estimated to be $0.5 \pm 0.1\mu_B$ by assuming that the magnetic domains of equivalent propagation vectors are equally populated. This value is close to the amplitude of the SDW in pure chromium [8]. The solid line in Fig. 3 represents the calculated structure factor. In the real space, this structure is a cycloid which turns in the a–c plane with a period of $1.76a$.

The present cycloidal magnetic structure differs from the SDW predicted by Liu *et al.* They neither predicted the possibility of the $[110]^*$ cycloid, nor did they calculate the generalized susceptibility for Q parallel to the $[110]^*$ axis. However, their Fermi surface geometry does not seem to reject a $[110]^*$ incommensurate structure. The magnetic neutron diffraction lines detected by Castaing are assigned satisfactorily to the satellites 000±, 100— and 001± of the present model. To refine the accuracy any more, it will be necessary to prepare single crystals enriched with ^{11}B.

We conclude that the magnetic structure of CrB_2 is basically cycloidal. The simple sinusoidal structure is rejected. However, more complex structures, an elliptical cycloid for example, are allowed within the present experimental accuracy.

Acknowledgments – We would like to express our thanks to Dr. Y. Ishizawa and to Dr. S. Kawai for their stimulating discussions and continuous encouragement. We are indebted to Mr. N. Minakawa for his assistance in neutron measurements.

REFERENCES

1. BARNES R.G. & CREEL R.B., *Phys. Lett.* **29A**, 203 (1969).
2. CASTAING J., COSTA P., HERITIER M. & LEDERER P., *J. Phys. Chem. Solids* **33**, 533 (1972).
3. CASTAING J., Thesis, University of Paris (1971).
4. LIU S.H., KOPP L., ENGLAND W.B. & MYRON H.W., *Phys. Rev.* **B11**, 3463 (1975).
5. TANAKA T., BANNAI E., KAWAI S. & YAMANE T., *J. Cryst. Growth* **30**, 193 (1975).
6. TANAKA T., NOZAKI H., BANNAI E., ISHIZAWA Y., KAWAI S. & YAMANE T., *J. Less-Common Metals.* **50**, 15 (1976).
7. STASSIS C., KLINE G.R. & SINHA S.K., *Phys. Rev.* **B11**, 2171 (1975).
8. SHIRANE G. & TAKEI W.J., *J. Phys. Soc. Japan* **17**, Suppl. B-III, 35 (1962).