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Neutron diffraction studies of transition metal nitrides

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Abstract. The magnetic structures of Fe_4N and Mn_4N have been redetermined using neutron diffraction. The magnetic form factors, obtained from polarised neutron data have been shown to be different for the face-centred and corner atoms. A qualitative explanation of the structures of Fe_4N and Mn_4N has been provided from the shapes of the magnetic form factors.

Keywords. Neutron diffraction; magnetic form factor; nitrides

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1. Introduction

Transition metal nitrides Fe_4N and Mn_4N exhibit interesting magnetic properties with ferro and ferrimagnetic ordering respectively. The crystal structure has space group Pm3m in which the metal atoms form a fcc matrix and the nitrogen atom occupies the interstitial body centre position (figure 1). The corner atom (M_I) has twelve metal atoms as its nearest neighbours at 2·69 Å whereas the face centre atom (M_{II}) has two

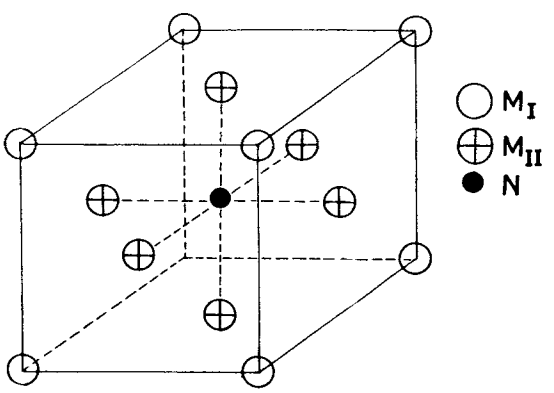

Figure 1. Unit cell of transition metal nitride M_4N.

†Since deceased.

nearest neighbour nitrogen atoms at 1·9 Å. Because of this difference in their environments, the corner and the face centre atoms show different magnetic properties.

These compounds have been extensively studied for their electronic and magnetic properties. Following the pioneering work of Guillaud (1953) and Wiener and Berger (1955) on these compounds, Frazer (1958) undertook a neutron diffraction study of Fe_4N and concluded that it is ferromagnetic with magnetic moments of 2·73 μ_B and 1·77 μ_B for the corner and the face centre atoms respectively. The Mössbauer measurements (Shirane *et al* 1962) show that the hyperfine fields at the corner and face centre atoms are approximately proportional to their magnetic moments of 3 μ_B and 2 μ_B respectively and the isomer shifts are in line with $3d^7\ 4s$ and $3d^8\ 4s$ configurations for the two sites. These configurations are derived from the assumption that the nitrogen acts as an electron donor to the face centre iron atoms. However, the electron diffraction (Nagakura 1968) yields the electronic configuration as $Fe_I^0(Fe_{II}^{1/3})_3N$.

Neutron diffraction studies on polycrystalline Mn_4N (Takei *et al* 1960; Takei *et al* 1962) show that it has a ferrimagnetic ordering with corner atom moment of 3·85 μ_B aligned antiparallel to the three face centre moments of 0·9 μ_B at 77°K. On the basis of neutron diffraction and neutron polarisation analysis (Bouchard 1968; Fruchart *et al* 1979) it has been claimed that Mn_4N has a noncollinear component of spin.

Mn_4N has been subjected to a variety of experimental measurements (Hisashi *et al* 1967; Mamoru 1966; Fruchart *et al* 1979) and it has exhibited anomalous magnetic and electronic properties. These observations have led to the band model calculations (Labbe and Jardin 1982; Jardin and Labbe 1975, 1983) based on a strong crystal field at the Mn_{II} site and a resonance between Mn and N electronic levels.

Regarding the magnetic structure of Fe_4N and Mn_4N, the existing literature appears to show an incomplete appreciation of the importance of the difference in the environments of the two species of metal atoms in these structures. The fact that the two atoms have significantly different environments leads to a difference in their magnetic moments. It should immediately follow that in the neutron experiments the atoms must also have different magnetic form factors. All the analysis so far have used the same magnetic form factors for the two sites, which leads to a serious flaw in the conclusions reached.

The present measurements are aimed at understanding not only the magnetic structures but the magnetic form factors in these compounds. The results on magnetic structures agree with the earlier results (Frazer 1958; Takei *et al* 1960). Interestingly, the magnetic form factors for the face centre Fe and Mn atoms in Fe_4N and Mn_4N respectively are found to be significantly different from those of the corner atoms.

2. Experimental

2.1 *Sample preparation*

Fe_4N was prepared by passing dry ammonia over 4N pure iron sponge, kept at 475°C, for 3 hr. The mixture of Fe_4N and Fe_3N thus formed, was heated in vacuum at 450°C for 4 hr. The resulting product was cubic γ' phase of Fe_4N, which was confirmed by x-ray analysis. For Mn_4N, nitrogen gas free of oxygen was passed over 4N pure manganese powder kept at 600°C. It was found necessary to crush the resulting product and repeat the heat treatment a couple of times to ensure a total reaction. X-ray analysis confirmed the formation of single phase Mn_4N.

2.2 *Neutron diffraction measurements*

The unpolarised neutron diffraction measurements were conducted at the TRIGA MARK II reactor PPTN Bandung, with neutron wavelength of 1·07 Å. Polarised neutron diffraction patterns were recorded using the polarised neutron spectrometer at the CIRUS reactor, BARC. This instrument has a wavelength of 0·92 Å and the polarisation and flipping efficiencies of 97·5% and 99·9% respectively.

3. Results and discussion

3.1 Mn_4N

The analysis of unpolarised neutron diffraction profiles shows that the structure is ferrimagnetic with magnetic moments of 3·50 μ_B and 0·89 μ_B for the corner and the face centre atoms respectively. The polarised neutron diffraction patterns are given in figure 2. Unpolarised neutron data is also shown for comparison. The depolarisation of the neutron beam in the sample was obtained by inserting the sample before the analyser crystal and measuring the polarisation of the neutron beam. From the polarised neutron intensities, the magnetic form factor for the face centred Mn atom was determined using Mn^+ form factor (Watson and Freeman 1961) for the corner atom. Figure 3 shows the experimental form factor for Mn_{II} along with the Mn^+ and Mn^{++} (Watson and Freeman 1961) form factors. The form factor for the Mn_{II} is sharper than that of Mn_I. This suggests that the unpaired electron distribution of Mn_{II} is much more spread out than that of Mn_I.

This is in agreement with the band model (Jardin and Labbe 1975, 1983; Labbe and Jardin 1982) for the transition metal nitrides and carbides. The model considers the

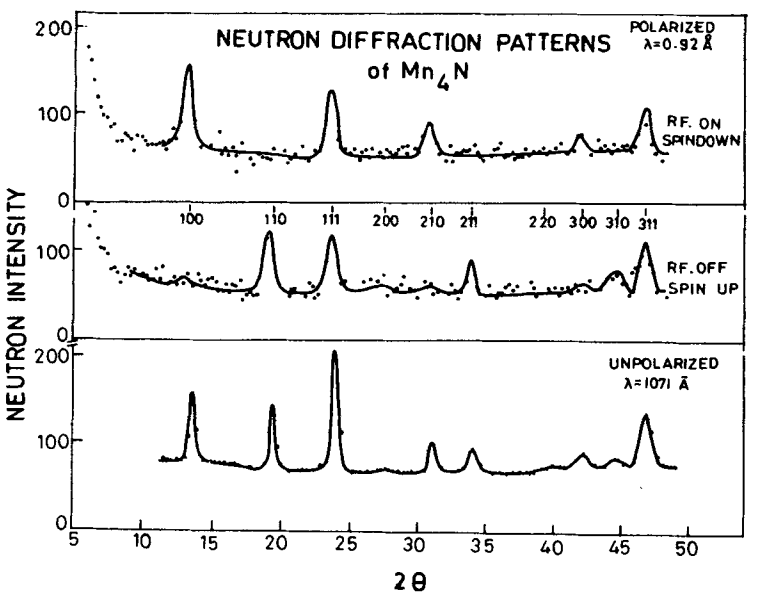

Figure 2. Polarised and unpolarised neutron diffraction patterns of Mn_4N.

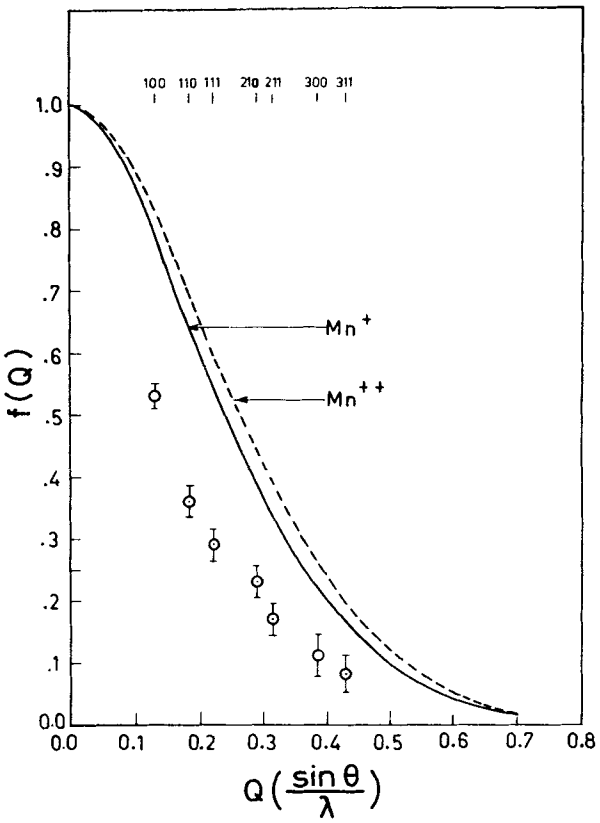

Figure 3. Magnetic form factor of face centre Mn atom in Mn_4N.

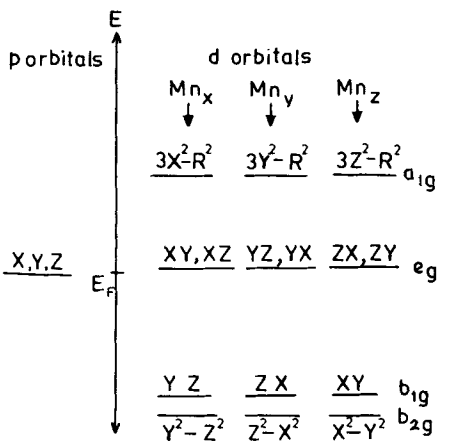

Figure 4. Crystal field levels of face-centred Mn (*d*-orbitals) and N (*p*-orbitals). E_F is Fermi energy (Labbe and Jardin 1982).

crystal field effects at Mn_{II} site. The site symmetry of Mn_{II} is D_{4h} with two nitrogens as nearest neighbours. The 3*d*-levels of Mn_{II}, in this strong crystal field, split into a_{1g}, e_g, b_{1g} and b_{2g} sublevels as shown in figure 4. Due to the large crystal field splitting, Hund's rule is not strictly valid and the magnetic moment is reduced. Further the *p*-level of nitrogen is in resonance with the d_{e_g} level of Mn_{II} resulting in the expansion of the unpaired electron density.

The experimental observations are thus in qualitative agreement with the theoretical model. The expanded moment density of Mn_{II} also implies an overlap of the unpaired electron distributions of Mn_I and Mn_{II}, favouring a ferrimagnetic alignment.

3.2 *Fe_4N*

The unpolarised neutron diffraction pattern of Fe_4N was recorded using neutrons of wavelength 1·07 Å. The intensities of various reflections were measured by applying a magnetic field parallel to their respective scattering vectors. The magnetic structure, obtained using this data, gave a ferromagnetic alignment with magnetic moments of 2·73 μ_B and 1·77 μ_B for Fe_I and Fe_{II} atoms. This is in agreement with the earlier neutron results on Fe_4N (Frazer 1958).

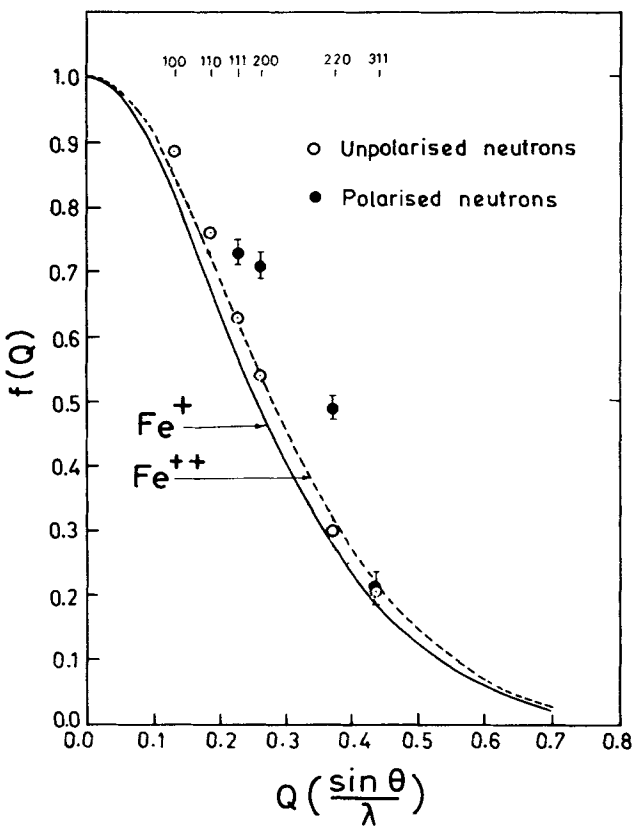

Figure 5. Magnetic form factor of face-centred Fe atom in Fe_4N. Unpolarised neutron data (open circles) gives an indication of the results discussed in the text.

The polarised neutron diffraction data on Fe_4N was analysed on lines similar to those of Mn_4N. The magnetic form factor for the Fe_{II} atom has been obtained from the intensities using Fe^+ (Watson and Freeman 1961) form factor for Fe_I and is shown in figure 5. The calculated Fe^+ and Fe^{++} form factors (Watson and Freeman 1961) are also shown for comparison.

The form factor for Fe_{II} is significantly expanded as compared to that of the corner Fe_I atom implying a contracted moment density for the Fe_{II} atoms. The unpaired electron densities of Fe_I and Fe_{II} are thus well localised and do not overlap leading to a ferromagnetic ordering between Fe_I and Fe_{II}. The reduction in the moment is probably due to the strong crystal field effects at the Fe_{II} sites modifying the electron density contributing to the magnetic moment.

4. Conclusion

The polarised neutron diffraction data analysed on the basis of different form factors for the two nonequivalent sites thus give a significant difference in the unpaired electron densities at the corner and the face-centred atoms. The experimentally determined moment densities have qualitatively been explained on the basis of an existing theoretical model.

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