$=ny^n$, we find

$$\mathfrak{D}_S\omega(x,a)=-\frac{1}{\Phi}\sum_{n=x}^{\infty}\left(\frac{1+\Phi}{\Phi}\right)^{n-x}y^n\prod_{p=-S}^{S}(n-p). \quad \text{(A6)}$$

We now take $a=0$ (or $y=1$), let $x=S+1$, and change variables from n to $m=n-S$, and from p to $r=S-p$. Then

$$\mathfrak{D}_S\omega(S+1,0)=\frac{-1}{\Phi}\sum_{m=0}^{\infty}\frac{(m+2S+1)!}{m!}\left(\frac{1+\Phi}{\Phi}\right)^m. \quad \text{(A7)}$$

Similarly, taking $a=0$, letting $x=-S$ and changing variables from n to $m=n-S-1$, and from p to $r=S+1-p$, we find

$$\mathfrak{D}_S\omega(-S,0)=-\frac{(1+\Phi)^{2S+1}}{\Phi^{2S+2}}\times\sum_{m=0}^{\infty}\frac{(m+2S+1)!}{m!}\left(\frac{1+\Phi}{\Phi}\right)^m. \quad \text{(A8)}$$

From Eqs. (A7) and (A8), we note that the ratio of the relevant quantities is

$$\mathfrak{D}_S\omega(-S,0)/\mathfrak{D}_S\omega(S+1,0)=(1+\Phi)^{2S+1}/\Phi^{2S+1}. \quad \text{(A9)}$$

Finally, inserting this ratio into Eq. (A1) gives Eq. (48).

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Electron Number of the Nitrogen Atom in Mn_4N

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In order to obtain some information about the effective electron number of nitrogen in Mn_4N, the x-ray atomic scattering factors of nitrogen and manganese were measured by Fe $K\alpha$ radiation. The experimental values of the scattering factor of nitrogen determined within a resultant probable error of 5% were close to the theoretical curve for N^0 or N^{1-}. This result contradicts the donor theory in which a nitrogen atom is supposed to donate electrons to the neighboring manganese atoms.

INTRODUCTION

RECENTLY, Takei *et al.*[1,2] have shown by a neutron diffraction study that the magnetic structure of Mn_4N is ferrimagnetic and is explicable in terms both of the donor property of nitrogen and of the energy splittings of manganese atoms caused by their local environments. In the donor theory which was proposed by Guillaud,[3] Wiener and Berger,[4] and Juza and Puff,[5] a nitrogen atom is supposed to donate one electron to each of the three face-centered manganese atoms.

In order to obtain some information about the effective electron number of nitrogen, the x-ray atomic scattering factors of nitrogen and manganese in Mn_4N were measured by Fe $K\alpha$ radiation for two samples supplied separately by Mekata and Takei, with the compositions $Mn_4N_{0.98}$ and $Mn_4N_{1.00}$, respectively, the latter of which contained a very small amount of MnO.

In Mn_4N, manganese atoms occupy the sites of a face-centered cubic lattice with a nitrogen atom at the body-centered position of the unit cell. There are four types of structure factor as follows:

$4f_{Mn}+f_N$ for all even indices, (1)

$4f_{Mn}-f_N$ for all odd indices, (2)

f_N for mixed indices with $h+k+l=$even, (3)

$-f_N$ for mixed indices with $h+k+l=$odd. (4)

The last two types of structure factor may be used for determining the values of the scattering factor of nitrogen in the range of small scattering angles, where the behavior of the scattering factor is more sensitively influenced by the total electron number of the relevant atom than in other angular ranges.

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RESULTS

The relative intensity values of all reflections were measured within an experimental error of 0.4—5.0% in the same way as described for MnO by the present authors.[6] Absolute intensities of three strong reflections, (111), (200), and (220), were measured within an experimental error of 1.0%, by a method essentially similar to that used by Batterman *et al.*[7] These absolute values were used to put the relative values on an absolute scale, the subsequent probable error being within 5%. The values of f_N, except for (100) and (110), and f_{Mn} were derived from the two sets of values representing (1) and (2), in the same way as for MnO.[6] Dispersion corrections were made to f_{Mn} using the values obtained by a previous study on MnO.[8] The experimental values of f_{Mn} and f_N thus obtained are shown in Fig. 1 and Table I. The values of f_{Mn} and f_N obtained from the relative measurements with Cu and Cr $K\alpha$ radiations could also be brought into good agreement with the values listed in Table I with a suitable scaling factor as well as with the known dispersion corrections.

In Fig. 1, in which the experimental values are compared with theoretical ones of f_{Mn} [9] and of f_N [10,11] in various states, the experimental values of f_{Mn} show a systematic deviation from any of the corresponding theoretical curves. This deviation may, of course, be largely accounted for by taking a suitable temperature factor, though there may remain a slight discrepancy due to the error in the scaling factor. Regardless of this ambiguity, it is conclusive that the experimental values of f_N, especially for the (100) and (110) positions, are close to the theoretical scattering factor curve for N^0 or N^{1-}.

TABLE I. Measured values for scattering factors of Mn and N with Fe $K\alpha$ radiation.

Reflection	f_{Mn}		f_N	
	$Mn_4N_{0.98}$	$Mn_4N_{1.00}$	$Mn_4N_{0.98}$	$Mn_4N_{1.00}$
(100)			5.9±0.2	5.8±0.2
(110)			4.9±0.2	4.8±0.2
(111)	17.6±0.4	17.8±0.4	4.2±0.4	4.3±0.4
(200)	16.5±0.4	16.7±0.4	3.6±0.4	3.6±0.4
(220)	13.1±0.4	13.3±0.4	1.8	1.4
(311)	11.5±0.5	11.7±0.5	1.9	1.6
(222)	11.0±0.5	11.2±0.5	1.9	1.7

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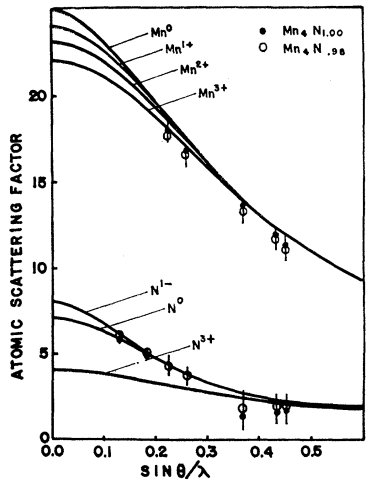

FIG. 1. Scattering factors for Mn and N. Solid lines are the theoretical curves without temperature factor corrections.

CONCLUSION

If, in accordance with the donor theory, the p-electron orbitals of nitrogen were to overlap the $3d$-electron orbitals of the adjacent manganese atoms to a significant extent, the p-electron density in the vicinity of the nitrogen position would decrease with respect to that of the neutral atom by some fraction of the three electrons, and the values of the atomic scattering factor in the range of $\sin\theta/\lambda = 0.1$ to 0.3 $Å^{-1}$ would be expected to lie somewhere between the values for a free neutral atom and those for N^{3+}. This inference is not in accord with the present result for f_N, even less so if the effect of the temperature factor is taken into account for nitrogen. In conclusion, the present result concerning the state of the nitrogen atom contradicts the donor theory. Similarly, there is no evidence that the acceptor theory suggested by Zener[12] for Fe_4N is valid either.

The scattering factor of Mn and the possibility that two kinds of Mn site exist will be discussed in detail in a subsequent paper.[13] Any difference between Mn atoms would have made one of the (100) or (110) reflections stronger and the other weaker. However, no difference seems to exist in view of the smooth behavior of the measured f_N values, and, therefore, the validity of the conclusion concerning the electron number of nitrogen is not affected on these grounds.

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