## LETTER TO THE EDITOR

## CALCULATED MAGNETIC MOMENT OF δ-MANGANESE

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Spin-density-functional theory is used to calculate the magnetic moment of δ-Mn whose ground state is assumed to be either antiferromagnetic or ferromagnetic. The band structure is given for paramagnetic, antiferromagnetic and ferromagnetic δ-Mn. The magnetic moment of antiferromagnetic δ-Mn is found to be $3\mu_B$ while that of ferromagnetic δ-Mn is $2.7\mu_B$. The total energy favors the antiferromagnetic ground state by about 0.3 eV.

Self-consistent spin-density-functional (SDF) theory has recently been extremely successful in calculations of the magnetic moments of the ferromagnetic metals Fe, Co and Ni [1–3]. But no application of SDF theory to antiferromagnetic metals has to the author's knowledge appeared in the literature to date.

The study of antiferromagnetic behavior of itinerant electrons was initiated by Slater [4] in 1951. The field was later thoroughly reviewed by Herring [5].

In this communication self-consistent band-structure- and SDF-theory is applied to the antiferromagnetic metal Mn. General points of view found in the literature [5] are supported by the results.

Manganese exists in four allotropic forms [6], but only one has a simple crystal structure which allows easy treatment with band structure theory. This is δ-Mn which has a bcc structure. Unfortunately, it exists only just below the melting point (1134 to 1245°C) and, therefore, its magnetic moment (if it exists) is not known. Goodenough [7] suggested that it is antiferromagnetic with a moment of about $1\mu_B$. Inspite of the justified objection that the calculations reported here are of a rather academic nature, δ-Mn is chosen because of its simple crystal structure and three calculations are carried out. Firstly, the ground state is assumed to be paramagnetic, secondly, antiferromagnetic and thirdly it is assumed to be ferromagnetic.

The method of calculation is the combined "compressed-atom augmented-spherical wave" method of Williams et al. [8]. The calculation for paramagnetic

Mn is performed with the local-density approximation of Hedin and Lundqvist [9]; the calculations for antiferromagnetic and ferromagnetic Mn are performed with the local spin-density approximation of von Barth and Hedin [10]. But the constants in their functional form are changed according to Janak [11] so that their exchange-correlation functional reduces to that of Hedin and Lundqvist in the paramagnetic limit. All calculations are iterated to self-consistency, the energies being stable to about 1 mRy and the magnetic moments to two significant figures.

Input to these calculations are the atomic number, the crystal structure, and the lattice constant. The latter can be varied so that the total energy is minimal. This, however, is not done in the present calculations and the experimental value of $a = 3.081$ Å [6] is assumed. For the calculation of ferromagnetic Mn the converged paramagnetic potential, $V$, is used to generate two potentials, $V\uparrow$ and $V\downarrow$, by initially applying a magnetic field. Spin-up and spin-down electrons are then essentially treated independently in the potentials $V\uparrow$ and $V\downarrow$, respectively [10]. The magnetic field is removed and in the following iterations the system relaxes to a new equilibrium. For the calculation of antiferromagnetic Mn, for the spin-up electrons the potential $V\uparrow$ is put e.g. on the cube corners and $V\downarrow$ in the body center of a CsCl-unit cell with the same lattice constant as bcc-Mn. For the spin-down electrons the same potentials are interchanged, i.e. $V\downarrow$ is put on the cube corners and $V\uparrow$ in the body center. The sys-
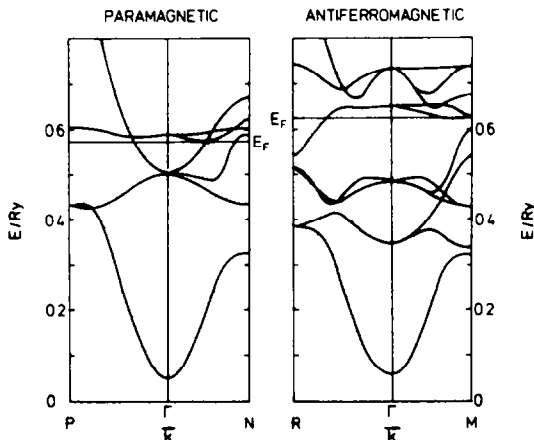
Fig. 1. Band structure along two symmetry axes for paramagnetic and antiferromagnetic Mn.



Fig. 3. Densities of states of paramagnetic Mn.

tem in the following iterations again relaxes to a new equilibrium.

The band-structures along two principal symmetry axes for paramagnetic (P-Mn) and antiferromagnetic Mn (AF-Mn) are shown in fig. 1. It is emphasized that, just like the bands of P-Mn, the bands of AF-Mn are manifestly spin-degenerate. The origin of the additional bands of AF-Mn compared with P-Mn is revealed in fig. 2: The bands of AF-Mn along ΓX arise from P-Mn along ΓH by folding the bands in the bcc-

Brillouin zone (fig. 2) into the sc-Brillouin zone, subsequently splitting the degeneracies and hybridizing states [5]. Thus, the second band of AF-Mn in fig. 1 arises from the first band of P-Mn along HP. The total density of states (DOS) and that of the d-electrons of P-Mn are shown in fig. 3. This is to be compared with fig. 4 which shows partial densities of states for AF-Mn. Fig. 4 must be read in two ways: for Mn in the cube corner, $Mn_{cc}$, say, it shows the spin-up DOS and that of spin-up-d electrons in the lower panel, the


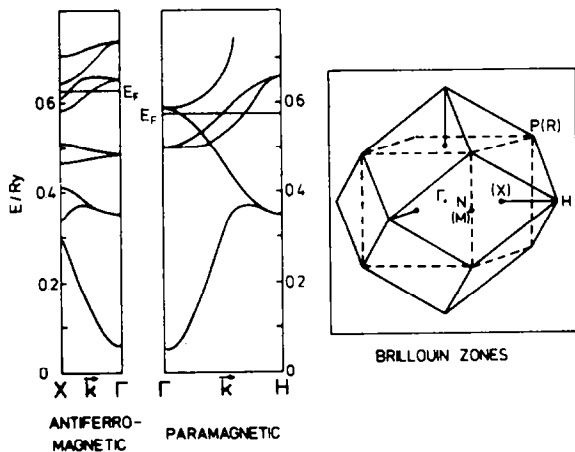
Fig. 2. Band structure along the [100]-axis for antiferromagnetic and paramagnetic Mn; Brillouin zone of the former dashed (symmetry lables in parenthesis), of the latter solid line.
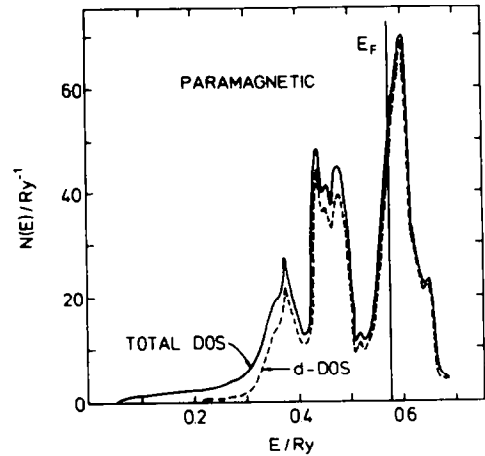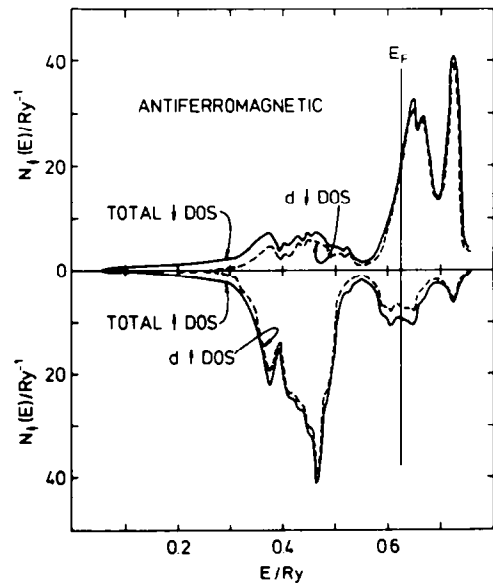


Fig. 4. Densities of states of antiferromagnetic Mn, see text.

spin-down DOS and that of the spin-down-d electrons in the upper panel. For Mn in the body center of the cube, $Mn_{bc}$, the lower panel applies to spin-down electrons and the upper to spin-up electrons. Therefore, fig. 4 equally well shows the site decomposed DOS of one spin direction only, e.g. that of the spin-up electrons on $Mn_{cc}$ in the lower panel and of the spin-up electrons on $Mn_{bc}$ in the upper panel and vice versa. While this statement may be self-evident, it nevertheless clarifies that the spin degeneracy in reciprocal space, which was emphasized in connection with fig. 1, in real space is achieved by placing two electrons of opposite spin in the same valence state, albeit on the two different atoms in the unit cell. Since the partial density of states, $N_{l\nu}(E)$, is defined by

$$N_{l\nu}(E) = \sum_k \delta(E - \epsilon^{(k)}) q_{l\nu}^{(k)},$$

where $\epsilon^{(k)}$ are the eigenenergies and the $q_{l\nu}^{(k)}$ are the $l$ and site $\nu$ (or spin) decompositions of the single electron norms associated with each eigenstate ($\sum_{l\nu} q_{l\nu}^{(k)} = 1$), fig. 4, when read as a site decomposition of the DOS, reflects the site asymmetry of the wave function of one spin direction.

In fig. 5 the band structure along two principle symmetry axes and the DOS of ferromagnetic Mn (F-Mn) are shown. Here the spin degeneracy is lifted resulting in majority and minority bands and corresponding DOS.

It was found earlier [3] that the calculated equilibrium lattice constants in SDF-theory are appreciably smaller than the experimental ones for the magnetic
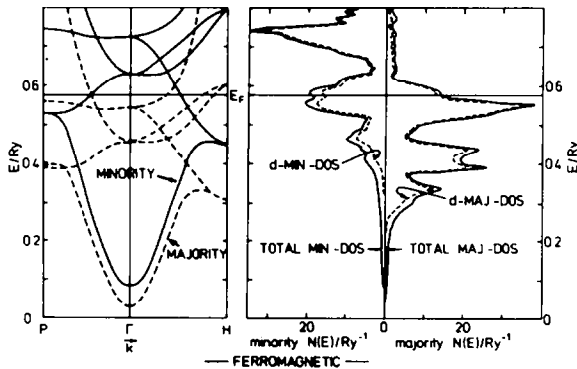
Table 1
Electronic pressure, $P$, exchange energy $I$, magnetic moment $\sigma_0$, and cohesive energy $E_c$

|        | $P$(Mbar) | $I$ (eV) | $\sigma_0$ ($\mu_B$) | $E_c$ (eV) |
|--------|-----------|----------|----------------------|------------|
| P-Mn   | −0.474    | –        | –                    | −3.97      |
| AF-Mn  | −0.204    | 0.42     | 3.05                 | −4.32      |
| F-Mn   | −0.297    | 0.43     | 2.75                 | −4.03      |

3d transition metals. The present results suffer from the same short coming of SDF-theory as is apparent from the first column of table 1 which shows a large negative pressure for P-Mn, i.e. theory predicts a smaller atomic equilibrium volume. The pressure is less negative for AF-Mn, the decrease being almost entirely due to the majority electrons (lower panel of fig. 4) which contribute −17 kbar. For F-Mn the majority electrons still contribute −66 kbar. The quantity $I$ of table 1 is an estimate of the exchange energy which is seen to be nearly the same for AF-Mn and for F-Mn. This estimate is obtained from one half the energy difference of the spin-polarized d-band-centers (the energies of the augmented Hankel functions in this theory [8]) divided by the magnetic moment which in table 1 is tabulated as $\sigma_0$. The magnetic moment is obtained by the difference between the integrated spin-up DOS and the spin-down DOS. The last column of table 1, finally, gives the cohesive energy which is obtained as the difference between the total energy of the solid and the total energy of the atom [3]. Since the atomic volume used is larger than the theoretical equilibrium value which, furthermore, will be different for P-, AF- and F-Mn (see the pressure), calculations at equilibrium will certainly change the values of the magnetic moment and more so, the values of the cohesive energies. The present calculations, however, show the antiferromagnetic ground state with a moment of $3\mu_B$ to have the lowest total energy.

## Acknowledgement

Fig. 5. Band structure of ferromagnetic Mn along two symmetry axes and partial densities of states.

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