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Calculation of Neutron and X-Ray Scattering Amplitudes for bcc Iron*

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The charge and spin densities for bcc iron were obtained from Bloch wave functions calculated by the augmented-plane-wave (APW) method. An iterative spin-dependent Hartree-Fock-Slater calculation was carried out and was found to yield a total spin per unit cell considerably in excess of the experimental value. The APW method was also applied to the potential of Wakoh and Yamashita, and the x-ray and neutron-scattering amplitudes were calculated from the resulting charge and spin densities for direct comparison with experiment. The neutron amplitudes are in reasonable agreement with experiment, and the calculated spin density confirms the existence of a region of negative magnetization density which has been inferred from experiment. The x-ray amplitudes for paired reflections indicate a much more nearly spherical charge distribution than do the experimental values. The sensitivity of these results to the potential used and the question of self-consistency have been investigated.

I. CALCULATION OF SCATTERING AMPLITUDES FROM BLOCH FUNCTIONS

In a periodic ferromagnetic crystal, the electronic spin density $\rho_s(\mathbf{r})$, the charge density of all occupied majority-spin states minus the charge density of all occupied minority-spin states, can be expressed as a Fourier series.

$$\rho_s(\mathbf{r}) = \sum_j c_j \exp(i\mathbf{K}_j\cdot\mathbf{r}). \tag{1}$$

In the absence of a contribution to the magnetization from the orbital motion of the electrons, the magnetic scattering amplitudes for the Bragg reflection of neutrons are proportional to the Fourier coefficients c_j.[1] The sum in Eq. (1) runs over all the vectors $\mathbf{K}_j$ of the reciprocal lattice and the positive direction for the spin density is defined in the scattering experiment by an applied magnetic field perpendicular to the scattering plane.[2] Similarly, the scattering amplitudes for Bragg reflection of x rays are proportional to the Fourier coefficients of the total charge density $\rho(\mathbf{r})$.

In the calculations presented here, the charge and spin densities of iron were calculated from the Bloch states of spin-dependent periodic one-electron potentials. One of these spin-dependent potentials was that of Wakoh and Yamashita[3] (WY) in which the spin dependence was introduced through a Slater $\rho^{1/3}$ exchange potential[4] modified by an adjustable parameter λ:

$$V_{\pm\mathrm{exch}}(\mathbf{r}) = -6(3/8\pi)^{1/3}\lambda[\rho(\mathbf{r})\pm\rho_s(\mathbf{r})]^{1/3}, \tag{2}$$

where the plus sign refers to states of majority spin and atomic units with energy in rydbergs are used. In the Green's-function energy-band calculation of WY, the choice $\lambda=0.5$, that is, Slater's exchange approximation cut in half, gave a self-consistent value of 2.2 Bohr magnetons (μ_B) for the spin magnetization per unit cell.[3] In our band calculation applying the augmented-plane-wave (APW) method[5] to this same potential, we reproduced the bands of WY to within 0.01 Ry and the energies of many of the states to within 0.001 Ry. To obtain the charge and spin densities we summed the charge densities of our majority- and minority-spin Bloch states up to a common Fermi level using a grid of 128 points in the Brillouin zone. In this way we found a total spin magnetization of $2.00\mu_B$. The discrepancy of $0.2\mu_B$ arises from the difference in methods of summing over occupied states. In the calculation of WY, the Green's-function method was used to obtain the energy bands along symmetry lines and then an interpolation based on tight binding functions for the d bands and plane waves for s bands was used to obtain the bands at other points. Thus, WY had the advantage of summing over a finer grid of points in the Brillouin zone but the disadvantage of inaccuracy in the s band resulting from the fitting procedure.

Because of the nature of the APW basis functions, the charge and spin densities obtained from the Bloch states are most conveniently expressed in terms of two different expansions which apply to different regions of the unit cell. In the interstitial region, defined to be the region outside touching spheres surrounding the atoms, the APW's are plane waves and since a finite number of these functions are used, the charge density of a state is given by a finite Fourier series. A similar Fourier series for the total charge or spin density is then obtained by summing over states and is convenient for obtaining a numerical tabulation of these functions in the interstitial region. Within the spheres, the Bloch functions are expanded in terms of radial functions and spherical harmonics so that it is convenient to express the square magnitude of the wave

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[1] G. T. Tramell, Phys. Rev. 92, 1387 (1953).

[2] C. G. Shull and Y. Yamada, J. Phys. Soc. Japan 17, Suppl. B-III, 1 (1962).

[3] S. Wakoh and J. Yamashita, J. Phys. Soc. Japan 21, 1712 (1966).

[4] J. C. Slater, Phys. Rev. 81, 385 (1951).

[5] J. C. Slater, Phys. Rev. 51, 846 (1937).

TABLE I. The first 27 Fourier coefficients of the calculated charge density c_1, and the calculated spin density c_2, resulting from our calculation using the WY potential are listed together with the experimental neutron diffraction results c_2', and the orbital contribution c_3 described in the text. Each coefficient is multiplied by the volume of the unit cell $\Omega = a^3/2$, where a is the cube edge of the bcc lattice. In these units $[\mu_B/(\text{unit cell})]$, the experimental uncertainties in c_2' are estimated to be ±0.013 for the first two Bragg reflections, ±0.0066 for the next two, and ±0.0052 for the remaining ones (Ref. 6).

$\mathbf{K}_j a/2\pi$	Charge Ωc_1	Spin Ωc_2	Expt. mag. $\Omega c_2'$	Orb. mag. Ωc_3	$\Omega[c_2' - c_3 - 1.07c_2]$
0 0 0	26.000	2.0000	2.2200	0.08	0.0000
1 1 0	18.371	1.2322	1.3964	0.0598	0.0182
2 0 0	15.124	0.7782	0.8969	0.0473	0.0169
2 1 1	13.033	0.4694	0.5546	0.0383	0.0141
2 2 0	11.536	0.3075	0.3852	0.0321	0.0241
3 1 0	10.409	0.2460	0.3044	0.0270	0.0142
2 2 2	9.628	0.1059	0.1365	0.0229	0.0003
3 2 1	8.977	0.0817	0.1015	0.0198	−0.0057
4 0 0	8.434	0.1206	0.1565	0.0169	0.0106
3 3 0	8.078	0.0225	0.0291	0.0147	−0.0097
4 1 1	8.052	0.0657	0.0828	0.0147	−0.0022
4 2 0	7.736	0.0305	0.0442	0.0129	−0.0013
3 3 2	7.487	−0.0273	−0.0362	0.0114	−0.0184
4 2 2	7.244	−0.0180	−0.0215	0.0100	−0.0122
4 3 1	7.045	−0.0248	−0.0291	0.0089	−0.0115
5 1 0	7.013	0.0320	0.0393	0.0089	−0.0038
5 2 1	6.698	−0.0065	0.0018	0.0073	0.0015
4 4 0	6.571	−0.0356	−0.0344	0.0067	−0.0030
4 3 3	6.450	−0.0534	−0.0604	0.0062	−0.0095
5 3 0	6.434	−0.0240	−0.0253	0.0062	−0.0058
4 4 2	6.327	−0.0485	−0.0435	0.0058	0.0026
6 0 0	6.290	0.0192	0.0262	0.0058	−0.0001
5 3 2	6.208	−0.0383	−0.0400	0.0056	−0.0046
6 1 1	6.183	0.0058	0.0113	0.0056	−0.0005
6 2 0	6.081	−0.0040	−0.0038	0.0054	−0.0049
5 4 1	5.997	−0.0379	−0.0415	0.0051	−0.0060
6 2 2	5.888	−0.0188	−0.0215	0.0050	−0.0064

function in the same form. In practice we need calculate only the parts of these two expansions which are invariant under the operations of the cubic group since the total charge and spin densities have the symmetry of the crystal. Finally, we can Fourier analyze functions represented by two such rapidly converging expansions and obtain a Fourier series representing the charge or spin density in the entire unit cell.

In Table I the neutron magnetic form factors,[6] scaled to the bulk magnetization of $2.22\mu_B$ per unit cell in the forward direction, are given together with the Fourier coefficients of our calculated spin density multiplied by the volume of the unit cell. One source of the difference between these two series is the orbital contribution to the magnetization which is inferred to be $0.08\mu_B$ per unit cell. This number comes from the bulk magnetization and the measured magnetomechanical ratio of $1.93\mu_B/\hbar$. Evaluation of the orbital contribution is beyond the scope of our nonrelativistic theory since time-reversal symmetry rules out the existence of any current density. That is, for each occupied state $\psi_{\mathbf{k}}(\mathbf{r})$, the state $\psi_{-\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}^*(\mathbf{r})$ is also occupied since $E(\mathbf{k}) = E(-\mathbf{k})$ and the current densities of these two states cancel. In order to obtain an orbital magnetization, it is necessary to consider spin-orbit coupling. The series for the orbital magnetization given in Table I was calculated using atomic wave functions and arbitrarily averaging the dependence of these form factors on the magnetic quantum number of the d orbital.[6]

The differences between the spin part of the experimental coefficients and our calculated Fourier coefficients of the spin density might have been considerably smaller if the parameter in the exchange potential had been adjusted to give a total spin magnetization of $2.14\mu_B$ per unit cell. If we estimate the effect of such a change in the potential by multiplying the calculated series by 1.07, then these differences become considerably smaller for the shorter scattering wave vectors as is shown in Table I. Thus our calculation does not establish any significant difference between the experimental spin density and that calculated with the type of adjustable potential described above.

II. NONSPHERICAL SPIN DENSITY

One interesting aspect of the neutron-diffraction data is that the scattering amplitudes for different wave vectors having the same magnitude are different. The differences between the amplitudes of these paired reflections are a direct measure of that part of the magnetization density which cannot be expressed as a lattice sum of spherically symmetric functions. One can obtain an approximate physical interpretation of these differences by assuming a model in which the

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[6] C. G. Shull (private communication).

TABLE II. Differences between coefficients of the spin density given in Table I for the five pairs of reflections having scattering vectors of equal magnitude.

$\mathbf{K}_1$	$\mathbf{K}_2$	$\Omega\Delta c_2'$	$\Omega\Delta c_2$	$1.07\Omega\Delta c_2$
4 1 1	3 3 0	0.0537	0.0432	0.0462
5 1 0	4 3 1	0.0684	0.0568	0.0608
5 3 0	4 3 3	0.0351	0.0294	0.0315
6 0 0	4 4 2	0.0697	0.0677	0.0724
6 1 1	5 3 2	0.0513	0.0441	0.0472

crystal spin density is a lattice sum of atomic spin densities which are nonspherical because of the partial occupation of the d shell. In this model, the difference between spin-density amplitudes for a paired reflection is[7]

$$\Delta c=[W_4(\mathbf{K}_1)-W_4(\mathbf{K}_2)](n_e-\tfrac{2}{3}n_t)\int_0^\infty P_{3d}^2(r)j_4(Kr)\,dr, \tag{3}$$

where n_e and n_t are the net numbers of spins in the t_{2g} and e_g d orbitals, respectively, $P_{3d}(r)$ is the assumed radial function for all d orbitals, K is the magnitude of the scattering vectors $\mathbf{K}_1$ and $\mathbf{K}_2$, W_4 is a suitably normalized cubic harmonic, and j_4 is the spherical Bessel function for $l=4$. From the values of Δc given in Table II we see that the calculated values are somewhat smaller than the experimental ones though by no more than 20%. If we "renormalize" the calculated values by multiplying by 1.07 to correct the total spin as before, the agreement is within about 10%, which is the approximate experimental uncertainty in these quantities.

III. NEGATIVE MAGNETIZATION DENSITY

Another interesting property of the spin density is that its sign is negative over a large portion of the interstitial region, i.e., the magnetization is pointing in the direction opposite to the bulk magnetization. One can gain some insight into this result by considering a pair of corresponding spin-up and spin-down Bloch states. By corresponding we mean that the states would coincide if there were no spin dependence in the potential. As one might expect from Eq. (2), the difference between the potentials for these two states is largest well inside the atom where the d orbitals responsible for most of the spin density are large. This spin dependence in the potential tends to pull the wave function of the majority-spin state toward the concentration of spin density inside the atom while pushing the wave function of the minority-spin state outward. Thus if both states are occupied, they make a positive contribution to the spin density within the atom and a negative contribution in the interstitial region. Since each majority state lies below the corresponding minority state, the calculated net spin implies that two majority states per unit cell have their corresponding minority states above the Fermi level. These states of course make a positive contribution to the spin density in the interstitial region which must be outweighed by the polarization of the pairs of corresponding occupied states if a region of negative spin density is to exist.

Since the negative spin density is quite small, having a calculated maximum value of -0.002 electron spins/cubic Bohr radius as compared with a value of 0.558 at the peak of the $3d$ function, it is difficult to get an accurate measurement of it since only a finite number of Fourier coefficients of the magnetization density are available from experiment. Similarly, the theoretical calculation of the spin density in the negative region involves considerable cancellation so that well-converged wave functions are required and a sufficient number of points in the Brillouin zone must be used. Having looked into the convergence of our Bloch functions and the matter of summing over the Brillouin zone, we find that the calculated negative spin density is significant. To ease the convergence difficulty in Fourier transforming the neutron data, a block-averaging procedure has been introduced in which one tries to evaluate the average spin density in a cube surrounding a given point rather than the value of the spin density at that point.[8] The sum which is then performed is

$$\bar{\rho}_s(\mathbf{r})=\sum_j c_j\exp(i\mathbf{K}_j\cdot\mathbf{r})\,\frac{\sin K_{jx}\delta}{K_{jx}\delta}\,\frac{\sin K_{jy}\delta}{K_{jy}\delta}\,\frac{\sin K_{jz}\delta}{K_{jz}\delta}, \tag{4}$$

where 2δ is the length of the edge of this cube. In Table III we present the block averages obtained from the experimental Fourier coefficients and from our calculated Fourier coefficients treated exactly the same way. In these comparisons the orbital contribution to the magnetization may be neglected since the block averages of this part are not significantly different from zero at the points in question. We also compare the truncated block averages at two points with the block averages of our finite Fourier series mentioned above and with the values of $\rho_s(\mathbf{r})$ at these points. From our numbers in the table we see that $\bar{\rho}_s(\mathbf{r})$ is somewhat different from $\rho_s(\mathbf{r})$ while the block averages obtained from the first 27 Fourier coefficients of $\rho_s(\mathbf{r})$ are reasonably accurate. Thus both the theory and experiment establish the presence of a region of negative spin density with its maximum value at the point $(a/2, a/4, 0)$ which is the point in the unit cell furthest from the atom.

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[7] R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959).

[8] C. G. Shull and H. A. Mook, Phys. Rev. Letters **16**, 184 (1966). The revised values for the block averages quoted here were presented by C. G. Shull at the Symposium on Neutron Scattering, 1967 AIME Annual Meeting, Los Angeles, California.

TABLE III. The calculated spin density $\rho_s(\mathbf{r})$ at points in the interstitial volume is compared with the block averages $\bar{\rho}_s(\mathbf{r})$ at these points and with the values of the block averages obtained from the first 27 Fourier coefficients. The numbers in the last two columns were obtained by carrying the sum in Eq. (4) out to each of the last 16 terms and then averaging these partial sums.

$\mathbf{r}$	$\rho_s(\mathbf{r})$	$\bar{\rho}_s(\mathbf{r})$	$\bar{\rho}_s(\mathbf{r})$ (27 terms)	$\bar{\rho}_s(\mathbf{r})$ expt. (27 terms)
$(\frac{1}{2}a\ 0\ 0)$	-0.000736	-0.000279	-0.000246	0.0013 ± 0.0010
$(\frac{1}{2}a\ \frac{1}{4}a\ 0)$	-0.002008	-0.001507	-0.001411	-0.0020 ± 0.0006
$[\frac{1}{2}a\ (5/32)a\ (5/32)a]$			-0.000765	-0.0013 ± 0.0006

IV. NONSPHERICAL CHARGE DENSITY

Some recent experimental information relating to the charge density consists of the ratios of the squares of the form factors for two paired reflections[9]:

$$f^2(442)/f^2(600)=1.05\pm0.01,$$

$$f^2(330)/f^2(411)=1.023\pm0.005.$$

The corresponding results from our calculations using the potential of WY are

$$f^2(442)/f^2(600)=1.0115,$$

$$f^2(330)/f^2(411)=1.0063.$$

Since the differences of these ratios from unity measure the nonspherical part of the charge density, we can see that the calculated nonspherical charge density is about four times smaller than that indicated by experiment.

It is of interest to see what effect a nonspherically symmetric potential within the atoms would have upon the nonspherical charge and spin densities. Well inside the atom, the asphericity of the charge and spin densities of the d shell will give rise to nonspherical terms in the Coulomb and exchange parts of the potential. Of these, the Coulomb term will tend to reduce the asphericity of the charge density while the exchange term will have the opposite effect. A comparison of these two terms, assuming the nonspherical charge and spin densities inferred from experiment,[9] and using Slater's approximation to estimate the exchange, indicates that the exchange effect may be the larger. We can get an idea of how such a perturbing potential would affect the charge density by finding its effect to first order on the energies, and hence the occupation of states near the Fermi level. From these estimates it appears that the effect of these nonspherical terms in the potential is several times too small to resolve the discrepancy in the nonspherical part of the charge density.

The amplitudes of the paired x-ray reflections indicate a preponderence of t_{2g} over e_g charge density greater than the 3:2 ratio which would give spherical symmetry. This implies a piling up of charge along the nearest-neighbor (111) directions and a depletion of charge along the (100) direction. If we consider the crystal potential at a given radial distance from the center of the atom, we expect the overlapping of neighboring atoms to lower the potential along the nearest-neighbor directions favoring a concentration of the charge density in these directions. Part of this qualitative aspect of the potential is suppressed by the "muffin-tin" approximation to the potential used in both the APW and Green's-function methods. If the potential used in the band calculation were allowed to vary in the interstitial region and depart from spherical symmetry within the atomic spheres, the calculated nonspherical charge density would presumably be enlarged by the overlap effect. Using a superposition of atomic charge densities, we have calculated a nonspherical potential arising from overlap. By estimating the effect of this nonspherical potential as above, we conclude that its effect on the calculated nonspherical charge density is also too small to account for the discrepancy.

V. SELF-CONSISTENT CALCULATIONS

Another matter bearing on the significance of our results is the sensitivity of these results to the spherical potential used inside the atomic sphere. One might hope that either the charge and spin densities would be much the same for various reasonable choices of the potential, or that the sensitivity of these functions to the assumed potential might be used in a semiempirical way to determine a suitable prescription for the crystal potential. Since such sensitivity is found to exist, we have considered a somewhat generalized Hartree-Fock-Slater (HFS) prescription in which the one-electron potential set up by a charge density $\rho(\mathbf{r})$ and a spin density $\rho_s(\mathbf{r})$ consists of the usual Coulomb part plus an exchange part of the form

$$V_{\pm\mathrm{exch}}=-6(3/8\pi)^{1/3}A[\rho(\mathbf{r})\pm B\rho_s(\mathbf{r})]^{1/3}, \qquad (5)$$

where the constants A and B are equal to unity for Slater's approximation. In our first series of calculations we used $A=B=1$ starting from a superposition of atomic charge and spin densities obtained from the

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[9] J. J. DeMarco and R. J. Weiss, Phys. Letters 18, 92 (1965).

TABLE IV. Summary of APW results for five different spin-dependent potentials. V_1 and V_4 are the first and fourth potentials, respectively, of the iterative HFS calculation. V_{WY} and V_{WY}' are described in the text and V_{WY}^* was obtained from the same charge and spin densities used to derive V_{WY}'. The zero of the energy scale on which the Fermi energy E_F is given corresponds to the constant majority-spin potential in the interstitial region. Q_{out} and S_{out} are the integrals of $\rho(\mathbf{r})$ and $\rho_s(\mathbf{r})$ over the interstitial region and the values of $\rho_s(\mathbf{r})$ are given in electron spins/cubic Bohr radius.

Potential	V_1	V_4	V_{WY}	V_{WY}'	V_{WY}^*
A	1	1	···	0.7	1
B	1	1	···	0.71	0.5
E_F	0.62133	0.59233	0.65670	0.69526	−0.00290
$\int_\Omega \rho_s(\mathbf{r})d^3r$	2.51566	2.68298	2.00000	2.00000	1.82813
Q_{out}	0.74201	0.82514	0.88353	0.93538	0.19988
S_{out}	−0.03914	−0.10166	−0.02166	−0.02221	−0.00572
$\rho_s(\frac{1}{2}a\ \frac{1}{4}a\ 0)$	−0.002747	−0.005458	−0.002008	−0.002018	−0.000499
$\rho_s(\frac{1}{2}a\ 0\ 0)$	−0.001713	−0.004601	−0.000736	−0.000741	−0.000385
$\rho_s(\frac{1}{4}a\ \frac{1}{4}a\ \frac{1}{4}a)$	0.001210	−0.000139	0.001211	0.001183	0.000355

HFS atomic program of Herman and Skillman.[10] After four iterations of this calculation, we found that the total spin magnetization per unit cell was $2.68\mu_B$ and was slowly increasing. In Table IV are listed some of the parameters characterizing the results of this calculation.

It would be of interest to know the results of self-consistent calculations using a wide variety of values for A and B, but such calculations are rather costly. The work of WY is not an example of such a calculation since the above self-consistent prescription was used in their calculation only to determine the difference between the one-electron potential to be used in the crystal and a free-ion potential for Fe$^+$. This free-ion potential was chosen to be the potential for which the Hartree-Fock radial 3d function satisfies the radial Schrodinger equation.[3] If we assume that the charge and spin densities of WY are correct, we can use them to determine the parameters in the exchange potential. To do this we use the charge density together with a Hartree-Fock core charge density to calculate the Coulomb potential. We then subtract this Coulomb potential from the WY potential and fit the remainder to the form of Eq. (5). This fitting procedure is easily reduced to the determination of one parameter by considering the difference between the spin-up and spin-down potentials expanded in powers of $\rho_s(\mathbf{r})/\rho(\mathbf{r})$:

$$\Delta V_{\mathrm{exch}} = -6(3/8\pi)^{1/3}A\rho^{1/3}(\mathbf{r}) \times\left[\frac{2B\rho_s(\mathbf{r})}{3\rho(\mathbf{r})}+\frac{10B^3\rho_s^3(\mathbf{r})}{81\rho^3(\mathbf{r})}+\cdots\right]. \quad (6)$$

Since $\rho_s(\mathbf{r})/\rho(\mathbf{r})$ is considerably less than 1 for all $\mathbf{r}$, the spin dependence of the potential is very nearly proportional to AB and since the spin dependence of the WY potential V_{WY} is given by Eq. (5) with $A=0.5$ and $B=1$, we choose $AB=0.5$. The choice $A=0.7$ and $B=0.71$ gave about as good a fit to V_{WY} as we could obtain using Eq. (5). As can be seen in Table IV, the spin density resulting from a band calculation with this new potential V_{WY}' is very close to that obtained from V_{WY} indicating that the fit to the spin dependence of the potential is very good. Using the slightly different charge and spin densities obtained for V_{WY}', we have calculated another potential V_{WY}'' with the same values of A and B. Since V_{WY}'' is even closer to V_{WY}' than V_{WY}' is to V_{WY}, we seem to have an approximately self-consistent calculation for this particular choice of exchange parameters.

As a check on the sensitivity of our results to the exchange approximation used, we have constructed a potential V_{WY}^* from the charge and spin densities of the WY calculation with $A=1.0$ and $B=0.5$. Since this exchange formula is the same as Slater's except for a weakening of the spin dependence, one might have expected it to yield results similar to those of our original HFS calculation but with a reduction of the calculated spin density. The energy band results from this potential, however, are drastically different from those mentioned above, having essentially all eight valence electrons in the d shell and thus a relatively small charge in the interstital region. The lack of conduction electrons is also shown by the Fermi energy which is much lower than both the HFS and WY Fermi energies, which are rather close to each other as can be seen in Table IV. A calculation of the potential set up by the charge and spin densities of this calculation shows that it is far from being self-consistent. In view of our earlier HFS results, it would seem that the exchange formula with $A=1.0$ and $B=0.5$ would give a much more reasonable band structure if it were carried to self-consistency.

VI. CONCLUSION

In our calculation using the potential of WY, we have found neutron-scattering amplitudes which are in

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[10] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

reasonable agreement with experiment and which might be brought considerably closer to experiment by a slight modification of the potential. We have also found that these results are close to self-consistency in the context of one modified HFS approximation ($A=0.7$, $B=0.71$) and far from self-consistency in another ($A=1.0$, $B=0.5$). On the other hand, the unmodified HFS approximation leads to a total spin per unit cell which is clearly too large. In contrast with the spin density, the calculated charge density has not shown sufficient sensitivity to the differences between potentials used in our calculations to account for the discrepancy in the x-ray scattering intensities.

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ac Magnetic Susceptibility and *H-T* Phase Diagram of $MnCl_2 \cdot 4H_2O$ between 0.26 and 1.50°K in Fields up to 27 kOe*

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The field-induced magnetic phase transitions in $MnCl_2 \cdot 4H_2O$ were investigated by measuring the differential magnetic susceptibility between 0.26 and 1.5°K in external magnetic fields up to 27 kOe. With the external field along the most preferred axis of the crystal (c' direction), both the antiferromagnetic-to-spin-flop (AF-to-SP) and the spin-flop-to-paramagnetic (SF-to-P) transitions were observed below 1.3°K. The AF-to-SF transition appears to be a first-order transition, as predicted by molecular-field theory. The temperature dependence of the phase boundary is given by $H_c=H_{c0}+bT$, where $H_{c0}=7550\pm10$ Oe and $b=434\pm10$ Oe/deg. Within the spin-flop state $\chi_{c'}$ is roughly constant and approximately equal to the value of $\chi_\perp$ in zero field. At the SF-to-P phase boundary, $\chi_{c'}$ drops rapidly to zero. The temperature dependence of the SF-to-P transition is given by $H_c=H_{c0}(1-CT^n)$ up to about 0.7°K, where $\mathrm{H}_{c0}=20.6\pm0.03$ kOe, $n=1.82\pm0.10$, and $c=0.228\pm0.002$.

MEASUREMENTS of the ac magnetic susceptibility of antiferromagnetic $MnCl_2 \cdot 4H_2O$ have been made in fields up to 27 kOe in the temperature range 0.26 to 1.5°K. Both the antiferromagnetic–to–spin-flop (AF-to-SF) and the spin-flop–to–paramagnetic (SF-to-P) phase transition boundaries were clearly determined from the data. These two phase boundaries together with the antiferromagnetic-to-paramagnetic (AF-to-P) boundary form a triple point at 1.30°K. The AF-to-SF critical field was found to fit the equation H_c (AF-to-SF) $=H_{c0}+bT$, where $H_{c0}=7550\pm10$ Oe and $b=434\pm10$ Oe/deg throughout the entire temperature range from 0.26 to 1.30°K. The best fit for the SF-to-P critical field up to 0.70°K was found to be H_c (SF-to-P) $=H_{c0}(1-CT^n)$, where $H_{c0}=20.6\pm0.03$ kOe, $n=1.82\pm0.10$, and $C=0.228\pm0.002$.

Single crystals of $MnCl_2 \cdot 4H_2O$ were grown by evaporation from saturated solutions at room temperature. $MnCl_2 \cdot 4H_2O$ has a monoclinic structure[1] with the angle $\beta=99°6'$. The crystals grow with the bc' plane prominent. The orientations of the crystal axes were determined by x-ray precession techniques. Most of the measurements were made with the external field parallel to the c' axis ($\perp$ to ab plane), and it is believed that this is the most preferred direction for this crystal.

The external field was produced by a superconducting solenoid. The differential susceptibility $\chi=dM/dH$ was determined by measuring the mutual inductance of a pair of coils surrounding the sample. A Cryotronics mutual inductance bridge was employed for these measurements. The coils were similar to those described by various authors[2,3] for magnetic temperature measurements at very low temperatures.

A He^3 refrigerator was used to obtain temperatures below 1.2°K. The temperature was determined by

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