

York, 1969). See also W. H. Louisell in University of Arizona, Optical Sciences Center Technical Report No. 31, 1969, Vol. II, p. 311 (unpublished).

¹¹J. H. Marburger and W. H. Louisell, Phys. Rev. **186**, 174 (1969).

¹²R. J. Glauber, Phys. Rev. **131**, 2766 (1963).

¹³K. E. Cahill and R. J. Glauber, Phys. Rev. **177**, 1857 (1969); **177**, 1882 (1969).

¹⁴J. C. Goldstein, Ph. D. thesis (MIT, 1971) (unpublished).

¹⁵L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967).

¹⁶See articles by M. E. Fisher and P. Heller, in

Reports on Progress in Physics, edited by A. C. Strickland (The Institute of Physics and the Physical Society, London, 1967), Pt. II.

¹⁷R. L. Stratanovich, *Topics in the Theory of Random Noise* (Gordon and Breach, New York, 1963) Vol. I, p. 66.

¹⁸L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 2nd ed. (Addison-Wesley, Reading, Mass., 1969).

¹⁹H. B. Callen, *Thermodynamics* (Wiley, New York, 1960), Chap. 15.

²⁰R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1965), p. 305.

Self-Consistent Calculation of Energy Bands in Ferromagnetic Nickel*

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A self-consistent calculation of energy bands in ferromagnetic nickel has been made using the tight-binding method. Eighty-nine points in $\frac{1}{48}$ th of the Brillouin zone were used to determine the charge density in the final stages of an iterative procedure. The Kohn-Sham-Gaspar exchange was employed. The approximately self-consistent potential was used to compute energy levels at 505 regularly spaced points in $\frac{1}{48}$ th of the Brillouin zone plus certain extra points close to the Fermi surface. Results are given for the density of states, the Fermi surface, the charge density, and the spin density. A magneton number of 0.58 was determined.

I. INTRODUCTION

This paper is an extension of a previous calculation of energy bands in ferromagnetic nickel using the tight-binding method¹ (Paper I). The work described in I was based on a crystal potential constructed from a superposition of overlapping neutral-atom charge densities, the atoms being in the $d^9 s^1$ configuration. The present calculation obtains an approximately self-consistent potential based on a sampling of the charge density at 89 points in $\frac{1}{48}$ th of the Brillouin zone. The procedure for achieving self-consistency has been described elsewhere.² Exchange has been included according to the $X\alpha$ method of Slater, Wilson, and Wood,³ however, it was found that the Kohn-Sham-Gaspar^{4,5} value of the coefficient $\alpha(\frac{2}{3})$ appeared to yield the most satisfactory results for the Fermi surface and other properties. This result is in marked contrast to the non-self-consistent calculation, in which it was found that a value of α close to that proposed by Slater ($\alpha=1$)⁶ was more satisfactory.

Separate exchange potentials are obtained for electrons of majority and minority (\uparrow and \downarrow) spins and energy bands are computed separately for the two spin states. This calculation is a test of the ability of such a procedure (the spin-polarized method) to account for the magnetic and electronic properties of a ferromagnetic metal. The results

are found to be in reasonable agreement with a variety of different experiments.

II. METHOD

The calculation employed the tight-binding method as reformulated by Lafon and Lin.⁷ The following set of basis functions was used: Atomic wave functions for all states except $3d$ (e.g., $1s$, $2s$, $3s$, $4s$, $2p$, $3p$, and $4p$) were represented by the linear combinations of Gaussian-type orbitals (GTO) determined by Wachters from a self-consistent-field calculation for the free nickel atom.⁸ It appears to be important to allow the d wave functions sufficient freedom to distort in the crystalline environment. To accomplish this, we used a set of five separate radial GTO for each type of angular dependence of the d functions. The orbital exponents used in defining these functions were the same as used by Wachters.⁸

This choice of basis functions leads to a 38×38 matrix problem at a general point of the Brillouin zone. The d - d portion is 25×25 , the p - p portion 9×9 , and the s - s portion 4×4 . With matrices of this size it is possible to obtain energy levels at a reasonably large number of points in the zone. Two such matrices, which refer to \uparrow and \downarrow spin, are obtained at each point.

The energy levels and wave functions from our previous non-self-consistent calculation¹ were

TABLE I. Some Fourier coefficients of potential. (a) $V_C(K)$ is the Fourier coefficient of the Coulomb potential, (b) ΔV_C is the change in V_C obtained during the iterations of the self-consistent calculations, (c) $V_{x\uparrow}$ is the total Kohn-Sham-Gaspar exchange potential for electrons of \uparrow spin, (d) $\Delta V_{x\uparrow}$ is the change in this quantity found in the self-consistent calculation, (e) $V_{x\downarrow}$ and $\Delta V_{x\downarrow}$ are the corresponding quantities for electrons of \downarrow spin.

K	$V_C(K)$	ΔV_C	$V_{x\uparrow}$	$\Delta V_{x\uparrow}$	$V_{x\downarrow}$	$\Delta V_{x\downarrow}$
[000]	-1.6871	-0.0796	-1.4091	-0.0917	-1.4000	-0.1093
[111]	-0.9690	-0.0955	-0.2630	+0.0150	-0.2532	0.0188
[200]	-0.8560	-0.0687	-0.1328	0.0210	-0.1246	0.0261
[220]	-0.6043	-0.0205	-0.0350	0.0062	-0.0334	0.0082
[311]	-0.5033	-0.0095	-0.0626	-0.0052	-0.0634	-0.0058
[222]	-0.4775	-0.0076	-0.0666	-0.0068	-0.0677	-0.0079
[400]	-0.3964	-0.0027	-0.0501	-0.0055	-0.0510	-0.0067
[331]	-0.3528	-0.0021	-0.0228	-0.0013	-0.0231	-0.0017
[420]	-0.3399	-0.0015	-0.0145	0.0000	-0.0146	-0.0001
[422]	-0.2972	-0.0008	0.0062	0.0030	0.0065	0.0035
[333]	-0.2715	-0.0006	0.0076	0.0029	0.0079	0.0034
[511]	-0.2710	-0.0001	0.0076	0.0029	0.0079	0.0034
[440]	-0.2368	-0.0001	-0.0048	0.0004	-0.0048	0.0005

used as input material for the first iteration of the self-consistent procedure. The procedure for calculating the change in the exchange potential described in Ref. 2 was modified as follows. The change in the Fourier coefficients of charge density was averaged over directions of \vec{K} , and the resulting Fourier series was summed to determine the change in charge density in an atomic cell for each spin direction. This was added to the starting charge density, the cube root was extracted, and a corrected exchange potential was formed. At first, our calculation employed a value of the exchange parameter α close to unity ($\alpha = 0.972$), which had been found to give the most satisfactory results. The charge density was sampled at 20 points in $\frac{1}{48}$ th of the Brillouin zone. Reasonably self-consistent results were obtained after about

eight iterations. The resulting energy bands appeared to be unsatisfactory, both in regard to the relation of the p and d bands, and in regard to the magneton number. Estimates were made which indicated that the exchange parameter α should be decreased. It appeared that $\alpha = \frac{2}{3}$ should be employed and the self-consistent calculations were repeated with this value. The results obtained in this case appeared to be in substantially better agreement with experiment.

Our experience with the effect of exchange on the band structure is similar to that reported by Connolly.⁹ We found, in agreement with Connolly, that if the full Slater exchange is used, the energy of the state L'_2 , for both spin directions, is above the Fermi energy. Hence there would be no Fermi surface neck at L . The reduction of the exchange potential produced by use of the Kohn-Sham-Gaspar value of the parameter α raises the d levels substantially more than those of p symmetry. The L'_2 levels are then below the Fermi surface, while the large spin splitting of the L_3 states forces L_3 above the surface. The criterion employed to define an adequate degree of self-consistency was that the Fourier coefficients of Coulomb potential should be stable to 0.002 Ry. For the case $\alpha = \frac{2}{3}$, eight iterations were made using 20 points in $\frac{1}{48}$ th of the Brillouin zone, followed by three iterations using 89 points. It was sufficient to consider only Fourier coefficients of potential for the 50 shortest reciprocal-lattice vectors in the iterative procedure to achieve self-consistency. Higher coefficients describe the charge density deep inside the core of an atom, and do not change appreciably. The convergence of the exchange potential is somewhat more rapid than that for the Coulomb potential. This is expected since the exchange potential varies only as the cube root of the charge density. Nu-

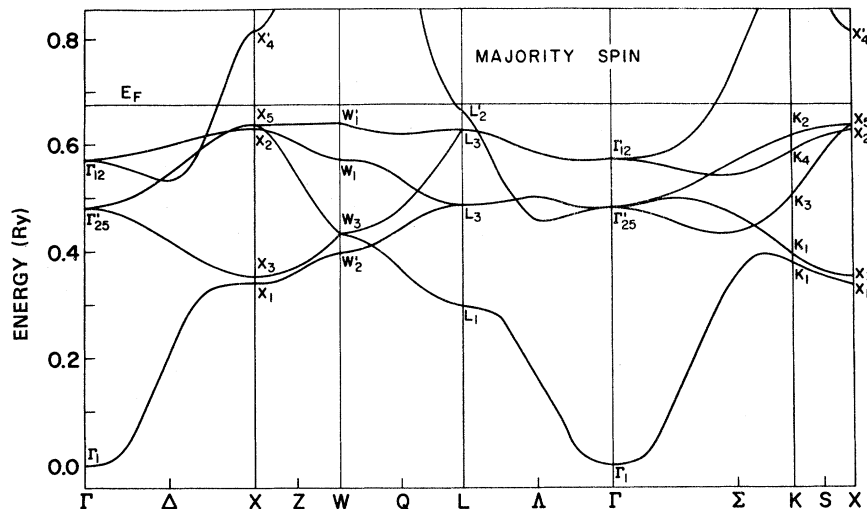


FIG. 1. Band structure for majority-spin states along certain symmetry directions. The horizontal line at 0.675 Ry indicates the position of the Fermi energy.

TABLE II. Energy differences for selected states (in Ry).

	Majority spin		Minority spin	
	Present	Ref. 9	Present	Ref. 9
$\Gamma_{25}' - \Gamma_1$	0.483	0.478	0.534	0.542
$\Gamma_{12} - \Gamma_{25}'$	0.091		0.095	
$X_5 - X_1$	0.300	0.330	0.323	0.362
$X_5 - X_2$	0.009		0.010	
$X_4' - X_5$	0.177		0.118	
$X_5 - \Gamma_1$	0.639	0.625	0.698	0.698
$X_4' - \Gamma_1$	0.816	0.841	0.816	0.842

d bandwidth: $X_{5\uparrow} - X_{1\uparrow} = 0.360$ Ry (4.9 eV)

merical values are presented for some Fourier coefficients in Table I.

After the self-consistent calculations had been completed, energies were computed at 505 points within $\frac{1}{48}$ th of the Brillouin zone. The density of states was computed from the energies by the Gilat-Raubenheimer method.¹⁰ Additional calculations of energy levels were made at a number of points close to the Fermi surface.

III. RESULTS: BAND PROPERTIES

The calculated band structure is shown in Figs. 1 and 2 for electrons of majority (\uparrow) and minority (\downarrow) along some symmetry directions. The bands have the expected shape, showing hybridization between the relatively narrow *d* band complex and a broad *s-p* band. Certain characteristic energy differences are listed in Table II. There is a substantial degree of agreement between our values for some of these separations and the corresponding results obtained by Connolly.⁹ Table II contains the results of Ref. 9 for those states for which energies are given in that reference. These energy

TABLE III. Exchange splitting of certain states at symmetry points (in Ry), according to the present (self-consistent) calculation, and as previously reported (Ref. 1).

State	Present	Ref. 1
	$E_{\downarrow} - E_{\uparrow}$	$E_{\downarrow} - E_{\uparrow}$
Γ_1	0.001	0.022
Γ_{25}'	0.052	0.060
Γ_{12}	0.057	0.063
X_1	0.038	0.049
X_3	0.044	0.054
X_2	0.060	0.065
X_5	0.060	0.066
X_4'	0.001	0.023
L_1	0.030	0.044
$L_{3(1)}$	0.052	0.060
$L_{3(2)}$	0.060	0.065
L_2'	0.000	0.020

differences are also in fair agreement with the results of Wakoh,¹¹ however, this author uses the full Slater exchange ($\alpha = 1$).

Exchange splittings of certain states are given in Table III. Results from the non-self-consistent calculation of I ($\alpha = 0.972$) are shown for comparison. It is seen that the splitting of states of predominately *d* symmetry has decreased slightly but not by as much as would have been expected in view of the decrease in α . There is significant variation in the amount of splitting from band to band. A striking result is that the splitting of states of predominately *s-p* symmetry is nearly zero. These results can be qualitatively explained in terms of the redistribution of spin density which will be discussed in Sec. IV. The spin polarization becomes negative (minority spin predominates)

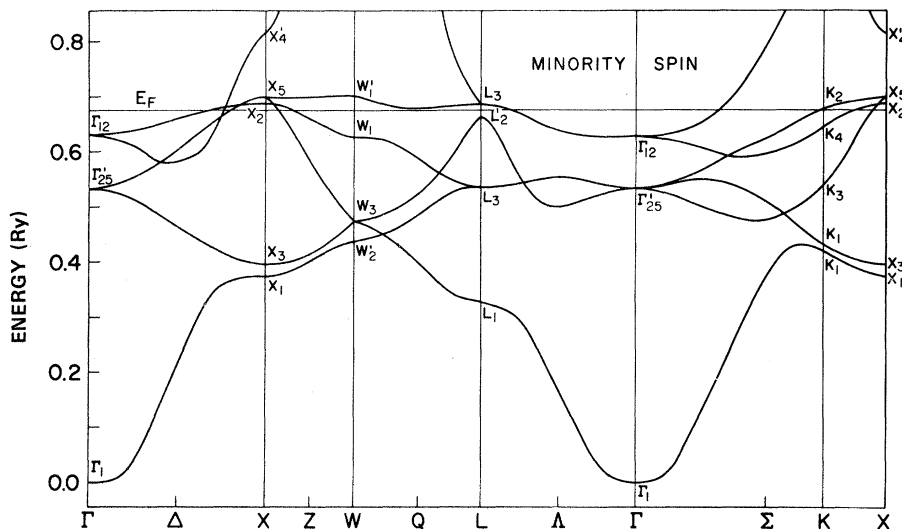


FIG. 2. Band structure for minority-spin states along certain symmetry directions.

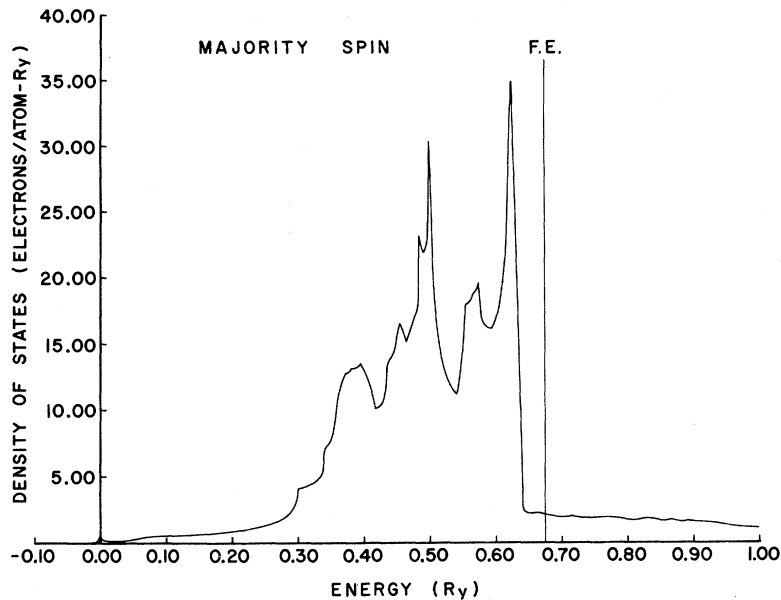


FIG. 3. Density of states for majority spin.

in the outer portions of the atomic cell. Highly extended states (s - p) experience cancellation of positive and negative exchange potentials. The more extended d states near the bottom of the band are also located on the average in a region of weaker exchange potential.

The densities of states for the majority and minority spins and their combination are shown in Figs. 3-5. These curves have the same general appearance as those presented in Ref. 1 except that the singularity structure is sharper, as a result of use of an improved method of calculation.

The Fermi energy was determined from the density of states. The magneton number, which is the difference between the number of occupied states of majority and minority spins, was found to be 0.58. This is reasonably close to the experimental value of 0.56.¹² The present result is a significant improvement over that obtained in the non-self-consistent calculation in which a value of 0.69 was reported. The total density of states at the Fermi energy is 23.5 electrons/atom Ry.

Determination of the Fermi energy makes possible investigation of the Fermi surface. Certain

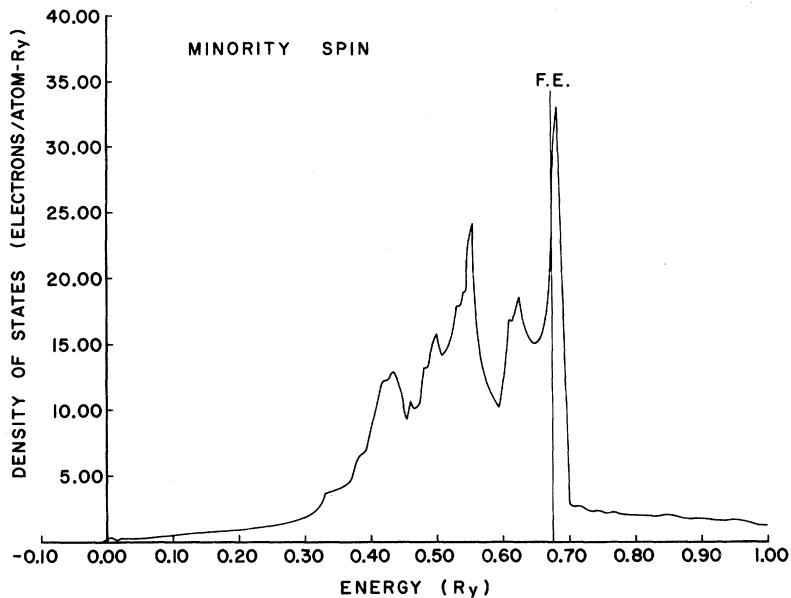


FIG. 4. Density of states for minority spin.

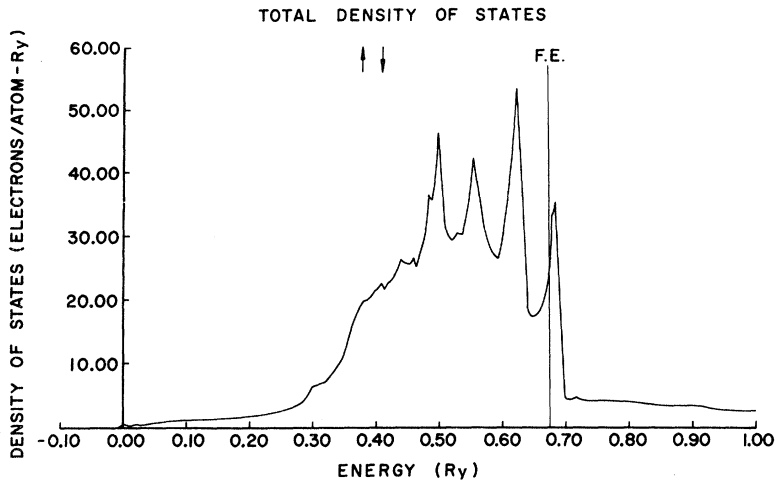


FIG. 5. Total density of states.

cross sections of the predicted Fermi surface are shown in Figs. 6 and 7 which refer to majority and minority spins, respectively. Some properties of the Fermi surface are listed in Table IV.

The majority-spin portion of the Fermi surface lies entirely in the upper *s-p* band (band 6). The surface is in contact with the Brillouin zone near the points *L*. A neck of roughly circular cross

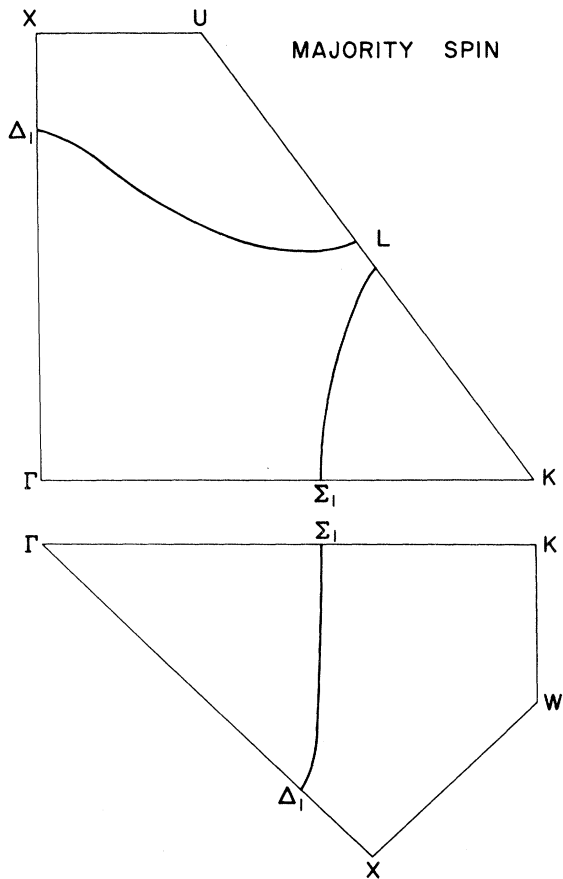


FIG. 6. Fermi-surface contours for states of majority spin in certain planes.

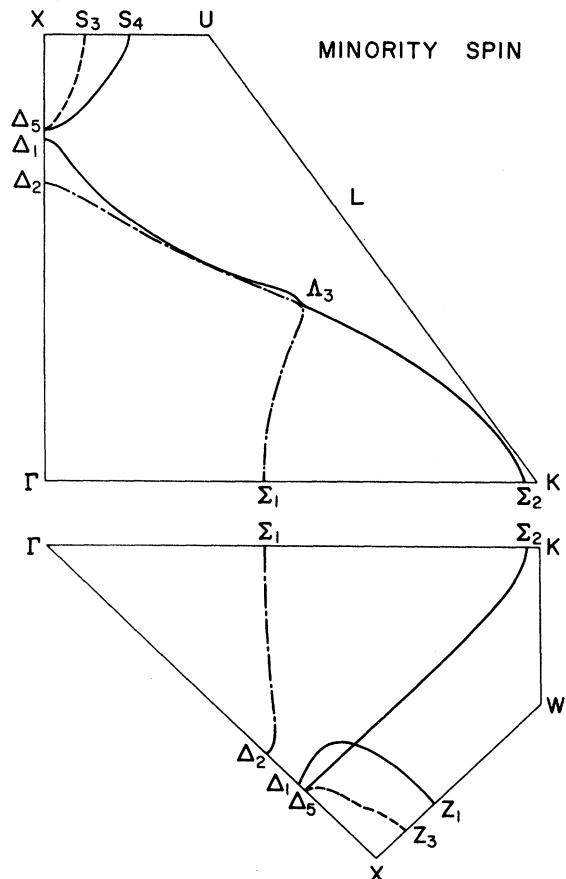


FIG. 7. Fermi-surface contours for states of minority spin in certain planes.

TABLE IV. Some properties of the Fermi surface. The area of the \uparrow spin s - p -band neck and linear \vec{k} -space dimensions of the X_5 , d -band hole pocket are given in a. u.

L_2 , neck extremal area	Theory	Expt. ^a
	0.068	0.072
$k_{X\Gamma}$	0.201	0.207
k_{XW}	0.078	0.099
k_{XU}	0.079	0.087

^aReference 13.

section is formed at each such point. We have computed the cross-sectional area of this neck in the hexagonal face of the zone. Our result (Table IV) is in good agreement with the measurements of Tsui.¹³

The minority-spin portion of the Fermi surface is considerably more complicated. It is predicted to contain components in four bands. There is strong mixing between the s - p band and the upper d bands of predominately t_{2g} symmetry. The simplest parts of the minority-spin surface are small hole pockets centered about X . These pockets have been observed in the de Haas-van Alphen effect.¹³ Our results for the size of these pockets are in moderately good agreement with experiment.

The rest of minority spin Fermi surface has not been observed. Other hole pockets should be found around X . Two large pieces are predicted. One is associated with the Γ_{12} level. This passes well in the interior of the zone. The wave functions associated with this piece have e_g symmetry on the $(1, 0, 0)$ and $(1, 1, 1)$ axes, but contain s - p components along the $(1, 1, 0)$ axis. The other is doubly connected, containing the majority of the d band holes responsible for the ferromagnetism of nickel. The latter is associated with the nearly flat upper d band of t_{2g} symmetry along the X - W line. In other directions, mixing with s and p orbitals is important. Changes in the symmetry of wave functions occur along the Fermi surface between symmetry points, so that a straightforward classification of large sheets in terms of a single symmetry is not possible. Additional complications arise when spin orbit coupling is considered, as pointed out by Zornberg.¹⁴ Further experimental investigation of the Fermi surface of nickel is important as a test of the predictions of band theory.

IV. SPIN DENSITY

The distribution of spin density in nickel has been investigated by Mook through neutron diffraction.¹⁵ This experiment determines a magnetic form factor, $f(\vec{k})$, which is the ratio of the magnetic scattering amplitude for a scattering vector

\vec{k} , to that for $\kappa=0$. This function has been computed by Hodges, Ehrenreich, and Lang using their combined tight-binding and pseudopotential interpolation method.¹⁶ It is customary to express $f(\vec{k})$ as the sum of three terms

$$f(\vec{k}) = \frac{2}{g} f_{\text{spin}}(\vec{k}) + \frac{(g-2)}{g} f_{\text{orb}}(\vec{k}) + f_{\text{core}}(\vec{k}),$$

in which g is the spectroscopic splitting factor. The quantity f_{spin} is the form factor for the unpaired (mainly d) electrons, and is normalized so that $f_{\text{spin}}(0) = 1$:

$$f_{\text{spin}}(\vec{k}) = (N\nu)^{-1} \int e^{i\vec{k}\cdot\vec{r}} [\rho\uparrow(\vec{r}) - \rho\downarrow(\vec{r})] d^3r,$$

in which ν is the magneton number. Although the core has a net spin of zero, exchange effects produce a slight difference in the radial distributions of \uparrow and \downarrow spin core electrons, and so, lead to a small contribution f_{core} . Finally, there is a contribution, f_{orb} from the possible unquenched orbital angular momentum of the d electrons. This term has been studied by Blume.¹⁷ However, the assumptions of his calculation are not in accord with

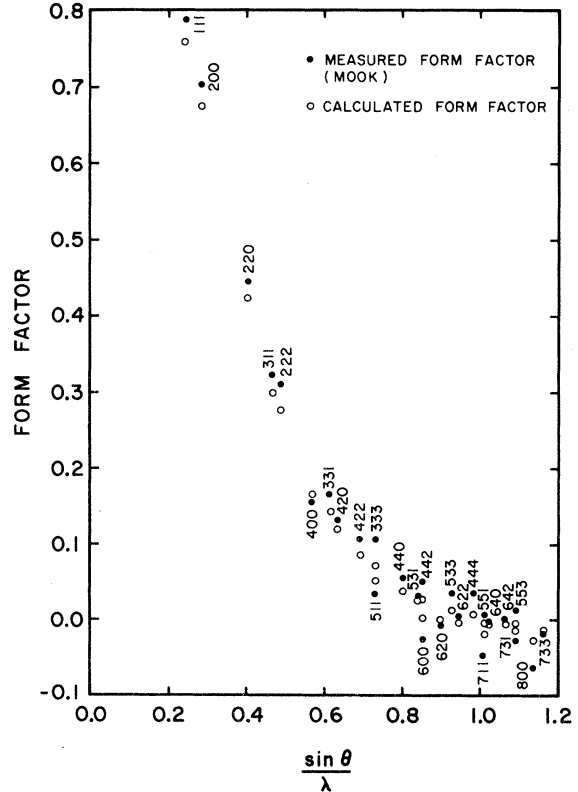


FIG. 8. Comparison of calculated and observed magnetic scattering form factors.

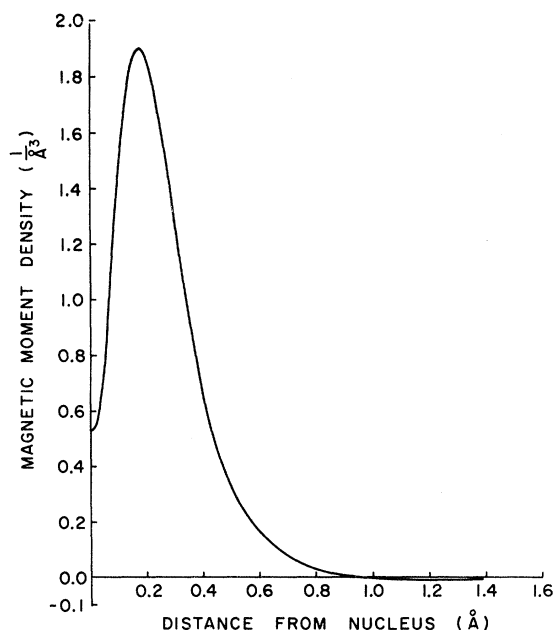


FIG. 9. Spherically averaged spin density in an atomic cell.

the band picture described here.

We have calculated the spin and core contributions to $f(\vec{k})$, using the wave functions obtained from our band calculation. The formulas are obtained immediately from Ref. 2. The results are shown in Fig. 8, where they are compared with the experimental values of Mook. A satisfactory, although not perfect degree of agreement is obtained. It will be noted that there can be considerable departures from spherical symmetry: $f(\vec{k})$ is not simply a function of $|\vec{k}|$, in agreement with experiment.

It is also of interest to examine the position dependence of the spin density. The spherically averaged spin density $\rho\uparrow(r) - \rho\downarrow(r)$ is shown in Fig. 9. It will be noted that this quantity is negative at large values of r , indicating that there is a net negative spin polarization in the outer portion of the atomic cell. This result is also in agreement with observation.

TABLE V. Atomic scattering factors for nickel. The present results are compared with experimental observations reported in Ref. 18.

$(a/2\pi)\vec{k}$	f (theory)	f (expt.)
[111]	20.38	20.10 ± 0.16
[200]	19.03	18.55 ± 0.16
[220]	15.36	15.34 ± 0.12
[311]	13.54	
[222]	13.03	
[400]	11.44	11.18 ± 0.11
[331]	10.50	
[420]	10.26	
[422]	9.38	
[333]	8.87	8.74 ± 0.09
[511]	8.91	8.73 ± 0.09
[400]	8.23	
[531]	7.92	
[600]	7.86	
[442]	7.81	

V. CHARGE DENSITY

The Kohn-Sham-Gaspar exchange prescription is based on a variational calculation of the total energy, regarded as a functional of the charge density. It is therefore particularly interesting to examine the results of our calculation with respect to the charge density. In this case, the theoretical results for the Fourier coefficients of the charge density can be compared with experimental observations of the x-ray atomic scattering factor by Diana, Mazzone, and De Marco.¹⁸ The results are presented in Table V. The small differences between the theoretical values for $\vec{K} \sim [333]$ and $\vec{K} \sim [511]$ and between $K \sim [600]$ and $K \sim [442]$ indicate slight departures of the charge distribution from spherical symmetry. Although there are deviations between theory and experiment which are outside the quoted experimental error, we feel that the agreement is fairly good. In the case of the [111], [200], and [220] vectors, our results are significantly closer to experiment than are values calculated from free atom Hartree-Fock charge densities for either $d^8 s^2$ or d^{10} configurations and reported by Diana *et al.*¹⁸

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¹J. Langlinais and J. Callaway, Phys. Rev. B 5, 124 (1972). This paper is referred to as I.

²J. Callaway and J. L. Fry, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1972), p. 512.

³J. C. Slater, T. M. Wilson, and J. H. Wood, Phys. Rev. 179, 28 (1969).

⁴W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

⁵R. Gaspar, Acta Phys. Hung 3, 263 (1954).

⁶J. C. Slater, Phys. Rev. 81, 385 (1951).

⁷E. Lafon and C. C. Lin, Phys. Rev. 152, 5971 (1966).

⁸A. J. H. Wachters, J. Chem. Phys. 52, 1033 (1970).

⁹J. W. D. Connolly, Phys. Rev. 159, 415 (1967).

¹⁰G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966).

¹¹S. Wakoh, J. Phys. Soc. Japan 20, 1894 (1965).

¹²H. Dannan, R. Heer, and A. J. P. Meyer, J. Appl. Phys. 39, 669 (1968).

¹³D. C. Tsui, Phys. Rev. 164, 669 (1967).

¹⁴E. I. Zornberg, Phys. Rev. B 1, 244 (1970).

¹⁵H. A. Mook, Phys. Rev. 148, 495 (1966).

¹⁶L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).

¹⁷M. Blume, Phys. Rev. 124, 96 (1961).

¹⁸M. Diana, G. Mazzone and J. J. DeMarco, Phys. Rev. 187, 973 (1969).

Relaxation Time of Superparamagnetic Particles with Cubic Anisotropy

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The superparamagnetic relaxation time is calculated for spherical particles with cubic magnetocrystalline anisotropy, whose easy axis is either [100] or [111] in zero applied field. Results are reported for relatively small particles only, in which no anomaly is found. It is concluded that the experimentally observed anomaly in this size region must be due to incoherent magnetization reversals.

I. INTRODUCTION

A magnetized ferromagnetic particle has to overcome an energy barrier before the direction of its magnetization can be changed. Since this barrier is proportional to the volume of the particle, the probability of a spontaneous flip of direction, by thermal agitation, is negligibly small for relatively large particles. However, if the particles are very small, thermal agitation can cause many changes in the direction of the magnetization in each particle during the time of measurement. An assembly of such particles will therefore reach a thermal equilibrium for the statistical distribution of magnetization orientations, and its measured magnetic properties will be similar to those of an ensemble of paramagnetic atoms. This phenomenon is called "superparamagnetism" and has been observed by many workers.¹

The usual theoretical study of the relaxation time associated with these thermal fluctuations¹ is based on the assumption that the magnetic moments of the particles are always in one of the two energy minima, and do not spend any time in between. Such a discrete orientation model leads to a relaxation time τ which can be approximated by

$$\tau = f_0^{-1} e^{E_B/kT}, \quad (1)$$

where T is the temperature, k is Boltzmann's constant, and E_B is the barrier energy. Different authors use different values for the parameter f_0 , but it is just taken as a constant, which varies roughly between 10^{10} and 10^9 sec^{-1} .

This vague approach has been put on a much sounder basis by Brown,² who considered the magnetization vector in each particle as changing its direction continuously, in response to some random forces. Brown still kept the conventional assumption that each particle is a "single domain,"

namely, that the magnetization vector is constant within each particle during all the stages of its reversal. But he did not use any other arbitrary assumption. By using the theory of stochastic processes for a white spectrum of agitation forces, he wrote a rigorous Fokker-Planck-type differential equation which yields the relaxation time as its eigenvalue. He also showed that for the case of a uniaxial anisotropy in zero applied field, the asymptotic value of the relaxation time (in the limit of a very large barrier compared to kT) is given by Eq. (1) in which f_0 is *not* a constant. Rather,

$$f_0 = 2K\gamma_0(\alpha/\pi)^{1/2}/M_s, \quad (2)$$

where K is the anisotropy constant, γ_0 is the gyromagnetic ratio, M_s is the saturation magnetization, and

$$\alpha = KV/kT, \quad (3)$$

where V is the volume of the particle. This asymptotic formula was later shown to be a very good approximation to the actual eigenvalue in uniaxial ferromagnets, down to α of the order of 1, without,³ or even with⁴ an applied magnetic field. This result is often quoted as a proof for the constancy of f_0 , which is not quite the case, although the difference is not always very significant.⁵

For materials with cubic anisotropy, no rigorous computations of the relaxation time have ever been tried; this seems necessary after many experimental studies of superparamagnetism in cubic materials have been published in recent years, in which the results are still analyzed by (1) with a *constant* f_0 . Moreover, in a recent experiment⁶ a case was found in which τ is not a monotonically increasing function of the particle radius. This effect was explained as resulting from incoherent rotation of the magnetization in the particle,⁶ which might or might not be an adequate explanation, but its theory