Hyperfine field of positive muons in Ni†

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We have calculated the contact hyperfine field of positive muons in Ni using a self-consistent spin-polarized density-functional formalism. Because we find more than an order-of-magnitude enhancement of the ambient hyperfine field at the muon position, it is impossible, within the confines of a free-electron model, to achieve agreement between neutron scattering results for the interstitial-polarization and muon-precession experiments. We propose a model in which the screening of the muon charge is done by free electrons of an essentially unpolarized $4s$ band, while the hyperfine field is due mainly to the relatively unperturbed $3d$ spin density arising from the different radial character of the majority and minority spin-$3d$ wave functions. This model can satisfactorily reconcile neutron scattering and muon-precession experiments and existing Ni band-structure calculations.

I. INTRODUCTION

In recent years a good deal of interest has been generated by the use of positive muons as probes of hyperfine fields in a wide variety of solids including magnetic materials,[1-3] nonmagnetic metals,[4] superconductors,[5] and spin glasses.[6] The basis of these experiments rests in the muon's asymmetric (with respect to its spin direction) decay into a positron and a pair of neutrinos. The positron is emitted preferentially in the direction of μ^+ spin at the moment of decay. If the muon is precessing due to either externally applied magnetic fields or due to the internal fields of the host in which it is stopped, the preferred direction of positron emission then oscillates in time. The number of positrons per unit time, emitted in a particular direction fixed in the laboratory frame, can be written

$$N(t) = N_0 e^{-t/\tau_\mu}[1 + a e^{-t/\tau} \cos(\omega t + \varphi)]. \quad (1)$$

Here N_0 is a normalization factor, $\tau_\mu = 2.2$ μ sec is the μ^+ lifetime, a is an anisotropy factor related to the weak decay and the initial polarization of the stopped muons, and φ is a phase angle dependent upon detector position. The two quantities of primary interest which are extracted from the experimental data are τ, the depolarization lifetime, and ω, the average muon precession frequency. It is ω with which we are concerned in this work.

$$\omega = 2\mu B_\mu/\hbar\ , \quad (2)$$

where μ is the magnetic moment of the muon and B_μ is the average magnetic field acting on the muon.

In magnetic metals such as Ni B_μ is determined partly by contributions easily calculated—externally applied fields, Lorentz fields, demagnetizing fields—and partly by contributions from internal fields such as dipole fields and the contact hyperfine field,

$$B_{\rm hf} = -\tfrac{8}{3}\pi[n_+(0) - n_-(0)]\,\mu_B. \quad (3)$$

Here μ_B is the Bohr magneton and $n_\pm(0)$ are the up- and down-spin densities at the muon site. In the case of Ni the muon is believed to be localized around a site with octahedral symmetry so that the dipole fields average to zero and $B_{\rm hf}$ is the only internal field of importance. An experimental measurement of ω then leads to a determination of $B_{\rm hf}$.

The advantages of the muon as a probe of internal fields are accrued basically from (i) its simple structure—a point ion with no core—and (ii) from the possibility of observing individual muon decays. In contrast to many NMR studies, for example, it is possible to reduce the perturbation of the host to the limit of infinite dilution. In some applications the dominant disadvantage of the probing muon is its positive charge. Thus while it is possible to reduce the number of muons present in a sample to extreme dilution, the local perturbation to the host of even a single μ^+ can be rather severe. One would naively expect this to be especially true in the measurements of hyperfine fields in a magnetic metal like Ni.

We usually want to extract from experiment a property of the host in the absence of the probe. However, $B_{\rm hf}$ fails to meet this criterion in a simple way because it depends upon presumably strongly perturbed spin densities at the position of a Coulomb singularity in the muon potential. Thus it is important to have a way of untangling a property of the pure system from a measured property of the system plus probe.

The most recent value[3] of $B_{\rm hf}$ in Ni is -0.64 kG, the minus sign indicating that $B_{\rm hf}$ results from a spin density oppositely directed to the bulk magnetization. It is of interest to note that $B_{\rm hf}$ corresponds almost exactly to the hyperfine field

one would predict if it were due only to the unperturbed spin density at the octahedral position in the unit cell, as measured by Mook.[7]

$$\mu_B(n_{0+}-n_{0-}) = -0.0085 \pm 0.004\ \mu_B/\text{Å}^3 . \tag{4}$$

The difficulty is then to understand how a necessarily large perturbation in charge density around the muon can lead to essentially no perturbation in spin density there.

A number of models have been proposed to explain this result. Jena[8] has developed an analytically soluble model, based upon earlier ideas of Daniel and Friedel,[9] in which the true Coulomb potential is replaced by a spin-dependent square-well potential. He adjusts the depth of the well to satisfy the Friedel sum rule and sets its range equal to the Thomas-Fermi screening length, while determining the spin splitting of the well depth from the interstitial magnetization data of Mook.[7] The negative-spin polarization of the neutron experiment is assumed to be totally due to the free 4s electrons. For Ni, Jena finds $B_{\rm hf} = -0.60$ kG, an agreement with experiment perhaps somewhat fortuitous in view of the crudity of the model.

Patterson and Falicov[10] have proposed a model for $B_{\rm hf}$ which is loosely based upon density-functional arguments. The principal assumptions are: (a) The muon hyperfine field is due only to the relatively free 4s electrons in the interior of the unit cell (as also assumed by Jena). (b) These are spin polarized oppositely to the bulk magnetization by antiferromagnetic exchange coupling to the more localized 3d electrons. (c) This exchange coupling may be replaced by a uniform exchange field H_e acting on the 4s electrons, thus eliminating the 3d electrons from the problem. The magnitude of H_e is chosen to yield agreement with the measured spin polarization far from the Ni ions, under the assumption that there are 0.6 4s electrons per site uniformly distributed over the unit cell.

Patterson and Falicov then applied crude density-functional arguments, and the additional assumption of linear screening of the muon charge, to calculate a relatively small enhancement of the ambient spin density at the muon site.

$$\rho_q(0) \equiv \frac{n_+(0)+n_-(0)}{n_{0+}+n_{0-}} \sim 5 , \quad \text{charge enhancement}$$
$$\rho_s(0) \equiv \frac{n_+(0)-n_-(0)}{n_{0+}-n_{0-}} \sim 1.4 , \quad \text{spin enhancement} . \tag{5}$$

The results of this calculation are rendered suspect by the use of linear screening, which is recognized to be a very poor approximation for Coulomb potentials.

Both of the above theories are based upon the screening of the μ^+ by a spin-polarized free-electron gas. In Sec. II we present the results of a more rigorous density-functional calculation of the spin and charge densities around the muon. We find disagreement with the conclusions of both Jena and Patterson and Falicov. In Sec. III we discuss the failure of the free-electron model of the hyperfine field and propose a new model involving both s and d electrons that is able to satisfactorily reconcile the neutron scattering data, the muon data, the results of Sec. II, and existing Ni band-structure calculations.

II. MODEL CALCULATION

We have carried out a full self-consistent density-functional calculation of the spin and charge densities around a muon embedded in a spin-polarized free-electron gas. Our procedure follows that used in spin-unpolarized density-functional calculations as originally introduced by Hohenberg, Kohn, and Sham[11,12] and extended by von Barth and Hedin[13] and Rajagopal and Callaway.[14] We have used the spin-dependent exchange and correlation potentials $v_{xc}^{\pm}$ of Gunnarsson, Lundqvist, and Wilkins.[15] All gradient terms are ignored so that the potentials depend only upon the local charge density and the local spin density.

$$v_{xc}^{\pm} = v_{xc}^{\pm}(r_S, \xi) , \tag{6}$$

where

$$n(r) = n_+(r) + n_-(r) = 3/4\pi r_s^3 ,$$
$$\xi(r) = [n_+(r) - n_-(r)]/n(r) . \tag{7}$$

The ambient value of the charge density is calculated to correspond to 0.6 4s electrons per nickel ion, and the ambient spin density is chosen to agree with Mook's[7] data.

$$r_{s0} = 3.2 ,$$
$$\xi_0 = 0.17 . \tag{8}$$

The radial Schrödinger equations to be solved for the scattering states are thus

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V^{\pm}\right) S_{kl}^{\pm}(r) = k_{\pm}^2 S_{kl}^{\pm}(r) , \tag{9}$$

while for the bound states which appear for $l = 0$ only

$$\left(-\frac{d^2}{dr^2} + V^{\pm}\right) S_B^{\pm}(r) = -\kappa_{\pm}^2 S_B^{\pm}(r) . \tag{10}$$

Here

$$V^{\pm} = -\frac{2}{r} + 2\int d^3\vec{r}'\ \frac{(\delta n_+(\vec{r}') + \delta n_-(\vec{r}'))}{|\vec{r}-\vec{r}'|} + v_{xc}^{\pm}(r_s, \xi) - v_{xc}^{\pm}(r_{s0}, \xi_0) , \tag{11}$$

$k_\pm$ is a wave vector below the Fermi surface and $-\kappa_\pm^2 = E_\pm$ is the energy of the bound state. The change in density from ambient is

$$\delta n_\pm(r) = n_\pm(r) - n_{0\pm} , \tag{12}$$

with

$$r^2\delta n_\pm(r) = \frac{1}{2\pi^2}\int_0^{k_F^\pm} k^2\, dk \times \sum_l (2l+1)[(S_{kl}^\pm(r))^2 - r^2 j_l^2(kr)] + [S_B^\pm(r)]^2 . \tag{13}$$

The first term above is the contribution of the scattering states to the density, and the second is the bound-state contribution. $S_{kl}(r)$ is normalized asymptotically to a phase-shifted spherical Bessel function and $S_B(r)$ is normalized to unity. The above equations are deemed self-consistent when the potentials $V^\pm$ calculated from the wave functions via Eqs. (11)–(13) are the same potentials which generated the wave functions in the first place through Eqs. (9) and (10).

In practice numerical approximations have to be applied to these equations. In agreement with others we found that they are extremely unstable, and we could not find an absolutely convergent solution. The difficulty derives from the long-range nature of the Coulomb interaction. One must program the solutions of the Schrödinger equation on the assumption that the potential falls asymptotically to zero faster than $1/r$ but any deviation from exact charge neutrality, i.e., $Z \neq 1$ where

$$Z = 4\pi \int_0^\infty [\delta n_+(r) + \delta n_-(r)] r^2\, dr \tag{14}$$

invalidates this assumption. Instead of correcting itself in a stable manner, a deviation from charge neutrality in one iteration tends to make the solutions on subsequent iterations oscillate wildly. We have overcome this difficulty only by forcing our solutions at each stage of interaction to obey Eq. (14). Below we outline the manner in which a qualified convergence was achieved.

The parameters of our program were as follows (i) Six values of l were employed to calculate the changes in density $\delta n_\pm(r)$. Since about 90% of the screening is due to $l = 0$ states, the error in truncating the l summation in Eq. 13 is very small. (ii) The integral in Eq. (13) was calculated using 30-point Gaussian quadrature. As described below solutions at $k = k_F^\pm$ were also generated, and these were used to check the Friedel sum rule. (iii) Equations (9) and (10) were solved on a 160 point mesh in the radial variable using the Numerov method.[16] Mesh size varied from 0.01 a.u. near the origin to 0.16 a.u. at large r, and the largest value of r was 25.39 a.u. (iv) Bound-state wave functions and energies were calculated using a modified Herman-Skillman[16] program. The phase shift, $\delta_l(k_\pm)$, of each scattering solution $S_{kl}^\pm$ was calculated, and the solutions at the Fermi surface were used to find the degree to which the Friedel sum rule was satisfied:

$$Z = \frac{1}{\pi}\sum_l (2l+1)[\delta_l(k_F^+) + \delta_l(k_F^-)] = 1 . \tag{15}$$

Since this sum rule must be satisfied by any self-consistent solution, we chose never to carry out a complete iteration unless we knew it would be satisfied. The technique used to enforce this was programmed as follows. On the first iteration a guess for $\delta n(r) = \delta n_+(r) + \delta n_-(r)$ generated the initial potentials.

$$\delta n(r) = (\alpha^3/8\pi)e^{-\alpha r} . \tag{16}$$

Since α is an adjustable parameter in the sense that any value satisfies Eq. (14) with $Z = 1$, we chose α by requiring that $V^\pm(r)$ yield solutions $S_{kl}^\pm(r)$ which satisfied the sum rule. Thus the first two iterations of the Schrödinger equation were carried out with potentials which fell to zero asymptotically faster than $1/r$.

On subsequent iterations we enforce the sum rule as follows. Initial potentials $V_n^\pm(r)$ for iteration n were calculated from the final spin and charge densities of the previous iteration. The Schrödinger equation was then solved only at the Fermi surface and the phase shifts were used to find Z. In general we found $Z \neq 1$ and would not carry out a full iteration until the starting potentials were modified. If $Z \gtrless 1$, indicating too much (little) charge accumulation, our potentials were correspondingly too attractive (repulsive). We then computed new potentials $V_{nf}^\pm(r)$ from densities slightly adjusted from the output of the previous interation.

$$\delta n_\pm \to f\,\delta n_\pm , \quad f \gtrless 1 \text{ if } Z \gtrless 1 , \quad f \lesssim 1 \text{ if } Z < 1 , \tag{17}$$

In practice f was unity to within a few parts in 10^4, but even this small change was sufficient to alter Z by several percent. A search for the proper f was made until $Z = 1$ within a small tolerance. When f was found the full iteration was carried out.

Our test for self-consistency was made on the initial and final potentials of each iteration. We required

$$|rV_{\text{init}}^\pm(r) - rV_{\text{final}}^\pm(r)| < \delta \tag{18}$$

at each of the 160 points in the r mesh. In practice we found that the smallest value of $\delta \approx 0.03$ was obtained after only three or four iterations. Further iteration resulted in poorer convergence.

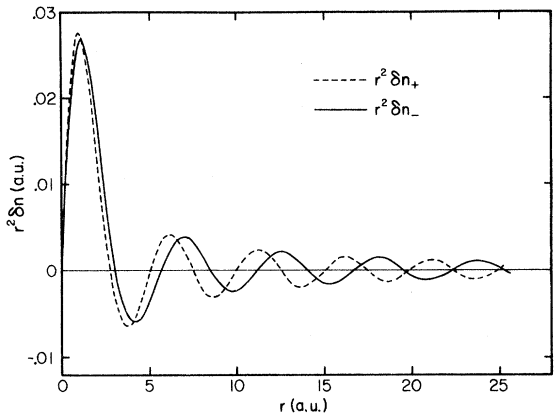

FIG. 1. Total excess majority-and minority-spin density as a function of distance from the muon.

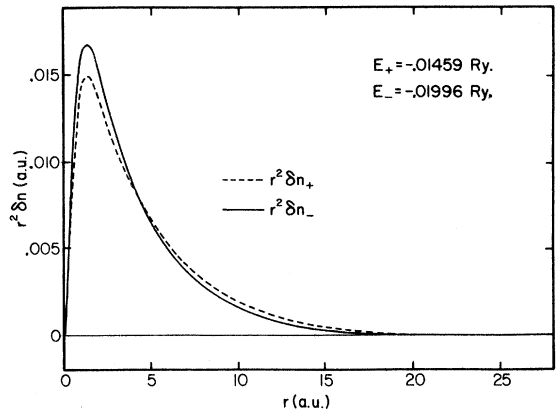

FIG. 2. Majority and minority bound-state density as a function of distance from the muon.

We feel that our final solution, while not absolutely convergent, is a good approximation to the exact solution. Near convergence, changes in density from one iteration to the next were typically 1% or less.

Our results are presented in Figs. 1—4. In Fig. 1 we have plotted the change in density as a function of distance from the muon for each spin orientation. For large r each orientation has its own characteristic Friedel oscillation period. Essentially all of the shielding charge is contained within about 3 a.u. of the origin—a distance less than but comparable to the nearest-neighbor Ni atoms in an actual crystal. From a Friedel phase-shift analysis we find that the total shielding charge contains a slight excess of minority-spin carriers. This fact is a direct consequence of the presence of bound states and will be commented on below.

The densities in Fig. 1 are the sum of both continuum and bound-state contributions. In Fig. 2 we have plotted separately the bound-state densities. The bound-state wave functions are relatively extended in space and it is not clear that they would be expected to survive the pertubation by nearby Ni ions. Even if they do not, we would expect that the overall change in density should be small. It should be noted that the minority-spin state is more tightly bound than the majority-spin state. The bound states thus make a negative contribution to the total spin density near the origin. Since the total spin density is found to be positive there, this is counterbalanced by a larger contribution of opposite sign due to the scattering states.

The presence of two bound states indicates that the muon looks more like an H^- ion from the point of view of the scattering states. There is thus apparently no tendency toward the formation of muonium, analogous to a neutral H atom, as is known to occur in semiconductors and insulators.

In Fig. 3 we have plotted the two final potentials $V^{\pm}(r)$. These drop essentially to zero within about 2.5 a.u. and then undergo small Friedel oscillations at larger distances. There is very little difference between V^+ and V^- near the origin, with V^- being slightly more attractive there. This near equivalence of the potentials together with the existence of bound states is sufficient to explain the slight predominance of minority-spin shielding mentioned earlier.

The total shielding charge is determined solely by the phase shifts $\delta_l(k_F^{\pm})$ of the continuum states at the Fermi surface. Defining $Z_{\pm}$ as the total number of excess majority (minority) carriers we have

$$Z_{\pm}=\frac{1}{\pi}\sum_l (2l+1)\delta_l(k_F^{\pm}), \tag{19}$$

with $Z_+ + Z_- = 1$. If the two potentials $V^{\pm}$ were in

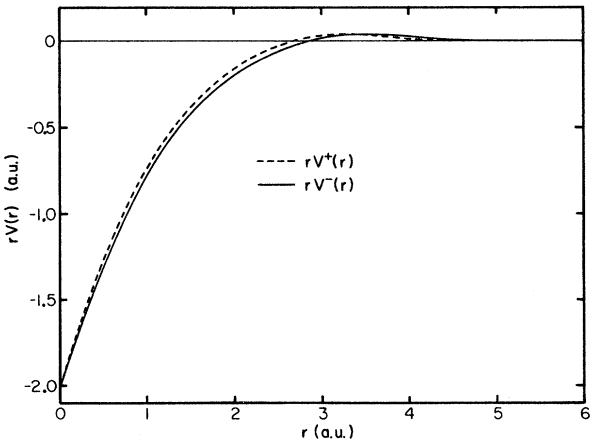

FIG. 3. Majority- and minority-spin self-consistent potentials as a function of distance from the muon.

fact exactly equal, $\delta_l(k)$ would be a single unique function of k for both spin orientations. The major difference between Z_+ and Z_- would then be due to the fact that $k_F^+ > k_F^-$. Our self-consistent solution shows that especially near the Fermi surface $\delta_0(k)$ is in fact nearly the same function for either minority or majority spins. The phase shift begins at π because of the presence of the bound states. This makes $\delta_0(k)$ a relatively rapidly-varying function of k since the Friedel sum rule requires that it drop from π to below $\frac{1}{2}\pi$ at the Fermi surface. In contrast the higher $l \neq 0$ phase shifts are all small and vary much less rapidly with k since $\delta_{l\neq 0}(0) = 0$. To a first approximation then the difference in the number of majority-spin and minority-spin shielding electrons is

$$Z_+ - Z_- \approx (1/\pi)[\delta_0(k_F^+) - \delta_0(k_F^-)]. \tag{20}$$

This is less than zero because $\delta_0(k)$ is a monotonically decreasing function of k. Note that if the bound states were absent, a similar argument would predict $Z_+ > Z_-$ since $\delta_0(k)$ would then be a monotonically increasing function of k.

Finally in Fig. 4 we have plotted our results for the spin- and charge-density enhancements $\rho_s(r)$ and $\rho_q(r)$. The charge density at the origin

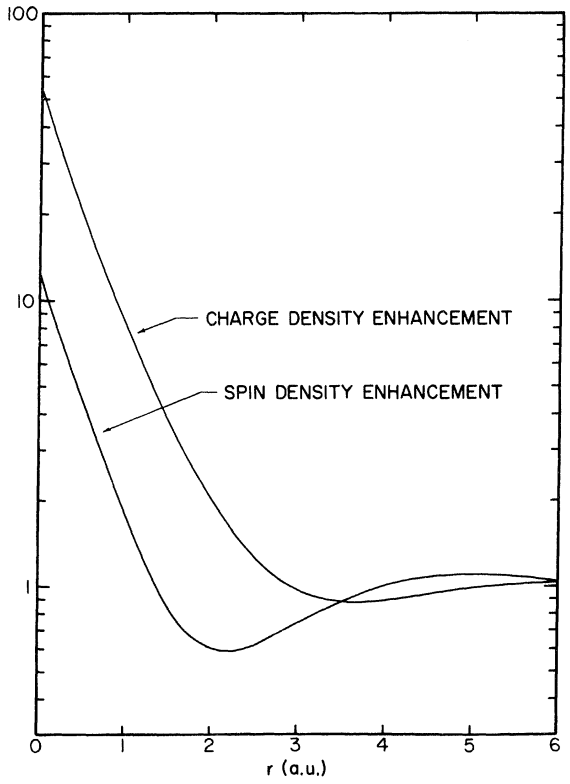

FIG. 4. Charge- and spin-density enhancements as a function of distance from the muon.

is approximately 54 times ambient, which is slightly greater than the density of a neutral hydrogen atom. The large value of $\rho_q(0)$ is not unexpected since in the limit $r_{s0} \to \infty$ we should find a solution for the H^- ion. In any event it is clear that the linear-response theory of Patterson and Falicov[10] is totally inadequate to treat such a large enhancement. If these authors had used $\rho_q(0) = 54$ instead of 5, their theory would predict $\rho_s(0) \approx 10$–15 instead of 1.4.

Although $\rho_s(0) \ll \rho_q(0)$ there is still a factor of 12.5 enhancement above the ambient spin density. This large spin density is in clear disagreement with the results of both Jena and Patterson and Falicov. It implies a hyperfine field more than an order of magnitude too large to explain the muon precession data. This large hyperfine field is the fundamental result of our calculation. We are led to conclude that a purely-free-electron model is incapable of reconciling the neutron-scattering data and the muon data. The manner in which we can reconcile these two experiments is discussed below.

III. DISCUSSION AND CONCLUSION

We consider first what happens if the input parameter ζ_0 is varied. In this connection we note that the neutron data gives us some latitude in the choice of ζ_0 since the quoted error in the spin polarization is about $\pm 50\%$.

We investigated this effect by setting $\zeta_0 = 0.06$ and solving self-consistently the new set of Schrödinger equations. We found the spin and charge enhancements at the origin to be essentially unchanged from the $\zeta_0 = 0.17$ calculation. This is intuitively understandable. The charge-density enhancement is primarily a function of the Coulomb potential and changes little due to magnetic effects. Also it is reasonable to expect that for small values of ζ_0, $n_+(0) - n_-(0)$ should be proportional to the ambient polarization $n_{0+} - n_{0-}$. Thus $\rho_s(0)$ should be constant, in agreement with our findings. We may summarize by setting

$$n_+(0) - n_-(0) = 12.5(n_{0+} - n_{0-}), \tag{21}$$

where this result is understood to apply to free electrons only. We conclude that even with the ambient polarization reduced by $\frac{1}{2}$ (the lower limit allowed by the neutron data), the free-electron hyperfine field is still much too large to agree with the muon experiments.

We thus postulate the following model for B_{hf} and investigate its consequences.

(a) The Ni s band is relatively unpolarized and does essentially all of the screening of the muon charge while contributing only a small amount

to the hyperfine field.

(b) The ambient polarization measured by neutron scattering is due mostly to the localized $3d$ functions and is essentially undisturbed by the screened potential of the muon.

The result of this model is a prediction for the muon hyperfine field which is close to that due to the ambient interstitial polarization in agreement with experiment. As justification for the model we note the following points.

There is considerable evidence from band-structure calculations that the s band in Ni is almost unpolarized. For example, Connolly[17] derives an average s band splitting of only -0.005 Ry, opposite to the much larger 0.07 Ry splitting of d bands. Callaway and Wang[18] find the s band splitting to be only $+0.001$ Ry while agreeing with Connolly in other details. The important point here is not the sign of the splitting but its extremely small value. In contrast, if the interstitial polarization is due totally to s electrons, as assumed by both Jena and Patterson and Falicov, the s-band splitting would be -0.08 Ry, a value in clear contradiction with the above band-structure estimates.

There is also agreement that a significant amount of negative spin polarization in Ni results from the different radial character of the majority- and minority-spin $3d$ wave functions. This possibility was already considered by Mook[7] as an alternative explanation of the negative interstitial spin density which he measured. The minority-spin d bands lie approximately one volt higher in energy than the majority-spin bands, causing the minority-spin wave functions to spread out more than the majority-spin wave functions. The net result is a negative spin density in the interior of the unit cell despite the smaller occupancy of the minority-spin states. In this connection we might note that Callaway and Wang,[18] while finding a small *positive* splitting of the s band, also find a *negative* spin density in interstitial regions of the unit cell. Duff and Das[19] have emphasized a similar point in their calculation of the band structure of Fe. With a relatively large and positive splitting (~0.1 Ry) of the s-p band they nonetheless find a negative spin density at certain interstitial positions in the unit cell. They conclude that these regions of negative polarization appear to be caused by a spin dependence of the radial part of the d-electron wave functions.

If we accept the proposition that the interstitial polarization is due primarily to $3d$ electrons, let us then consider the effects of the screened muon potential on them. If the s electrons are polarized to only a small amount, this potential will be approximately spin independent and any change in the d spin density must result from the different energy and range of the majority- and minority-spin d wave functions. We suppose this change is small and estimate it in perturbation theory. In the absence of the muon let H_0 be the Hamiltonian of the nickel lattice. H_0 possesses a complete set of eigenstates labeled by a band index n, wave vector $\vec{k}$, and spin σ satisfying

$$H_0\Psi^\sigma_{nk} = E^\sigma_{nk}\Psi^\sigma_{nk}. \tag{22}$$

In the presence of the muon we may write the change in Ψ^σ_{nk} to first order in perturbation theory as

$$\delta\Psi^\sigma_{nk} = \sum_{n'k'} \frac{V_{nk,n'k'}\Psi^\sigma_{n'k'}}{E^\sigma_{nk} - E^\sigma_{n'k'}}, \tag{23}$$

where

$$V_{nk,n'k'} \equiv \int d^3\vec{r}\, V(\vec{r})\, \Psi^{*\sigma}_{n'k'}(\vec{r})\, \Psi^\sigma_{nk}(\vec{r}) \tag{24}$$

and $V(\vec{r})$ is the spin-independent screened muon potential. $V_{nk,n'k'}$ will be small since it is only the tails of the wave functions which overlap a region of large $V(\vec{r})$.

The change in spin density is then

$$\begin{aligned}\delta n_\sigma(\vec{r}) &= 2\mathrm{Re}\sum_{n,\,k<k_F} \Psi^{*\sigma}_{nk}(\vec{r})\,\delta\Psi^\sigma_{nk}(\vec{r}) \\ &= 2\mathrm{Re}\sum_{n,k}\sum_{n',k'} \frac{V_{nk,n'k'}}{E^\sigma_{nk} - E^\sigma_{n'k'}} \Psi^{*\sigma}_{nk}(\vec{r})\,\Psi^\sigma_{n',k'}(\vec{r}) f(E^\sigma_{nk}),\end{aligned} \tag{25}$$

where $f(E)$ is the Fermi function. Interchanging the (n,k) and (n',k') summations and taking $\frac{1}{2}$ the sum of the result with Eq. (25) yields

$$\begin{aligned}\delta n_\sigma(\vec{r}) = \mathrm{Re}\sum_{n,k}\sum_{n',k'} V_{nk,n'k'}\,\Psi^{*\sigma}_{nk}(\vec{r})\,\Psi^\sigma_{n'k'}(\vec{r}) \\ \times\left(\frac{f(E^\sigma_{nk}) - f(E^\sigma_{n'k'})}{E^\sigma_{nk} - E^\sigma_{n'k'}}\right).\end{aligned} \tag{26}$$

Note that we may exclude the s band from the summations above since these bands have already resulted in the screened muon potential.

Consider the perturbation to the up (majority) spin density. Band-structure calculations indicate that these d bands are already full, so that the typical energy denominator above must be very large—the states $\Psi^\sigma_{n'k'}$ must correspond for example, to a $4p$ band. The smallness of the screened-potential matrix elements will then guarantee $\delta n_+ \approx 0$.

Although a similar argument for the minority-spin bands will yield only a small value for $\delta n_-(r)$ due to high lying bands, there is also a new contribution which comes from the unoccupied states of the corresponding $3d$ bands. Consider this con-

tribution in a model in which a single $3d$ band crosses the Fermi energy. We may drop the n subscript in Eq. (26) and, since the d bands are relatively flat, write

$$\frac{f(E_k)-f(E_{k'})}{E_k-E_{k'}}\approx\frac{df(E_k)}{dE_k}. \tag{27}$$

Then

$$\delta n_-(r)\approx \mathrm{Re}\sum_k\sum_{k'} V_{kk'}\,\Psi_k^{*-}(\vec{r})\,\Psi_{k'}^{-}(\vec{r})\frac{df(E_k)}{dE_k}. \tag{28}$$

The neutron-scattering results reveal that the $3d$ band wave functions are quite localized so that we approximate them by a tight-binding form

$$\Psi_k(\vec{r})=\frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\varphi_d(\vec{r}-\vec{R}), \tag{29}$$

where $\varphi_d(\vec{r}-\vec{R})$ is an atomiclike $3d$ orbital centered on site $\vec{R}$. Consider the matrix element $V_{kk'}$.

$$V_{kk'}=\int d^3\vec{r}\,V(\vec{r})\frac{1}{N}\sum_i e^{-i\vec{k}'\cdot\vec{R}_i}\varphi_d^*(\vec{r}-\vec{R}_i)\times\sum_j e^{i\vec{k}\cdot\vec{R}_j}\varphi_d(\vec{r}-\vec{R}_j). \tag{30}$$

The largest integrals have $i=j$ with i a nearest-neighbor site to the muon. Thus

$$V_{kk'}\approx\frac{1}{N}\sum_{\vec{\delta}} e^{i(\vec{k}-\vec{k}')\cdot\vec{\delta}}\Delta, \tag{31}$$

where $\vec{\delta}$ is a nearest-neighbor distance and

$$\Delta=\int d^3\vec{r}\,V(\vec{r})\,|\varphi_d(\vec{r}-\vec{\delta})|^2, \tag{32}$$

which we take to be independent of $\vec{\delta}$. Then

$$\delta n_-(\vec{r})\approx\mathrm{Re}\sum_k\sum_{k'}\frac{1}{N}\sum_{\vec{\delta}} e^{i(\vec{k}-\vec{k}')\cdot\vec{\delta}}\Delta\Psi_k^{*-}(\vec{r})\times\Psi_{k'}^{-}(\vec{r})\frac{df(E_k)}{dE_k}. \tag{33}$$

Upon doing the $\vec{k}'$ summation and noting that the amplitude of $\Psi_k^-(\vec{r})$ at the muon site is again only due to the nearest-neighbor $3d$ orbitals we find the simple result,

$$\delta n_-(\vec{r})=\mathrm{Re}\frac{\Delta}{N}\sum_k\frac{df(E_k)}{dE_k}\sum_{\vec{\delta}}|\varphi_d(\vec{r}-\vec{\delta})|^2$$

$$=-[N_-(E_F)\Delta]\,n_{0-}(\vec{r}). \tag{34}$$

Here $N_-(E_F)$ is the density of $3d$ minority-spin states in energy per atom at the Fermi surface and $n_{0-}(\vec{r})$ is the ambient spin density of the band under consideration at the muon site. With the neglect of interband mixing this result is easily generalized to an arbitrary number of bands which cross the Fermi surface. Note that $\Delta<0$ so that we calculate an enhancement of the minority-spin density at the muon position.

For the validity of our perturbation theory we require

$$N_-(E_F)\,|\Delta|<1. \tag{35}$$

The Fermi level in Ni falls close to a large peak in the minority-spin density of states. Specific-heat measurements[20] yield a total density of states, including s and d electrons of both spin orientations, of about 3 states/atom eV. Subtraction of the s-state contribution and the effects of electron-phonon and electron-electron enhancement may leave $N_-(E_F)\sim 2$ states/atom eV. Using this estimate we then require

$$|\Delta|<0.5\ \text{eV}. \tag{36}$$

Equation (34) is suggestive of a more general result which can be justified by more rigorous nonperturbative calculation. There are two ways in which the $3d$ polarization can be changed by the muon. The first arises from a distortion of the $3d$ wave functions. Such a distortion is generated by mixing in excited states corresponding to higher-lying bands. We have argued that this effect will be small for both minority and majority spins because of the relatively large energy denominator in Eq. (26).

A change in polarization can also result from a local increase in the occupancy of otherwise unoccupied states near the muon. It is this effect which is contained in Eq. (34). To see this we note from Eq. (32) that Δ is essentially the change in energy of a $3d$ orbital which is a nearest neighbor to the muon. Thus for small Δ, $N_-(E_F)|\Delta|$ is just the excess number of minority-spin electrons attracted to the muon potential. We can view this as resulting from a local lowering in energy by an amount $|\Delta|$ of the $3d$ density of states on sites near the muon, such that normally unoccupied states become filled.

With this interpretation it is clear that only a small increase in minority-spin polarization near the muon is possible through this mechanism. Even if Δ is large enough to completely populate the minority-spin $3d$ states near the muon (an increase from 4.4 to 5 electrons per Ni atom), we would expect an increase of only 0.6/4.4 or 14% in the minority-spin polarization. In this connection we note that band-structure calculations[13,14] show the highest minority-spin $3d$ states to lie less than 0.5 eV above the Fermi level. Thus for Δ of this size the fractional increase in polarization due to occupancy effects should be quite small. In the absence of detailed knowledge about suitable tight-binding orbitals, it is difficult to make a reliable

estimate of Δ. However, it seems clear that for reasonable values we can anticipate only a moderate rise in $3d$ polarization in contrast to the large increase in $4s$ polarization noted in Sec. II.

If we ignore the small changes in d spin density, the total spin density at the μ^+ site can then be written

$$n_+(0) - n_-(0) = n_{0\,d+} - n_{0\,d-} + 12.5(n_{0\,s+} - n_{0\,s-}) , \tag{37}$$

where we have incorporated the results of Sec. II in the last term. Given the neutron scattering data and the muon data we can now use Eq. (37) to make an estimate from experiment of the Ni s-band splitting Δ_s. For a splitting small compared to the Fermi energy we have

$$\Delta_s = (4\pi^2/k_F)(n_{0\,s+} - n_{0\,s-}) . \tag{38}$$

$n_+(0) - n_-(0)$ in Eq. (37) is determined by the muon data and $n_{0d+} - n_{0d-} + n_{0s+} - n_{0s-}$ by the neutron data. Given the quoted error of $\pm 0.004/\text{Å}^3$ in the neutron scattering result we find

$$\Delta_s = 0 \pm 0.003 \text{ Ry} . \tag{39}$$

This small value is in agreement with the results of the Ni band-structure calculations and provides added confirmation of our model.

In conclusion we find that a model for the muon hyperfine field in Ni which ignores the spin polarization of the $3d$ orbitals is not tenable. Conversely if the shielding of the muon is done by an unpolarized $4s$ band, the muon hyperfine field accurately reflects the interstitial host magnetization density due to the spin-polarized $3d$ orbitals. Our results suggest that the μ^+ experiments are in basic agreement with other theoretical and experimental results for Ni, and that the muons provide a useful way to differentiate between s- and d-band contributions to the interstitial magnetization, which is not possible by neutron scattering alone.

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