courtesy in providing the NiO sample. We also wish to express our appreciation to Dr. J. Appel for his continuing interest in this work and for many fruitful conversations on all theoretical aspects of the work.

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SPIN DENSITY OF s ELECTRONS IN IRON

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Recently Overhauser and Stearns[1] (OS) have interpreted Mössbauer measurements[2] on Fe-Al alloys. They concluded that there is a large qualitative difference between the true $4s$-electron susceptibility and the free-electron susceptibility $\chi_0(q)$ due to interactions between $4s$ electrons. The main purpose of this note is to argue that their conclusion is premature since their neglect of the k dependence of the periodic part of the $4s$ Bloch functions is probably serious. Although our treatment of this effect is not intended to be quantitatively accurate, it does indicate a considerable sensitivity of the results to such k dependence, and suggests that a detailed theory neglecting s-s interactions might indeed give approximate agreement with experiment.

Following OS, we consider the theory of s-d exchange, obtaining Yosida's[3] Eq. (2.14) to first order, from which one finds the spin density at lattice site $\vec{R}$ to be

$$S(\vec{R}) = \int \exp(i\vec{q}\cdot\vec{R})\sigma(\vec{q})d\vec{q}, \qquad (1)$$

$$\sigma(\vec{q}) = \frac{V}{4\pi^3} \sum_{\substack{\vec{k} \\ k < k_F}} \frac{u_{\vec{k}}(0)^* u_{\vec{k}+\vec{q}}(0)}{\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}} I(\vec{k}+\vec{q}, \vec{k}); \qquad (2)$$

V = crystal volume, $u_{\vec{k}}(0)$ is the periodic part of the Bloch function $\psi_{\vec{k}}$, evaluated at a nucleus,

and $\epsilon_{\vec{k}}$ is the energy associated with $\psi_{\vec{k}}$. Also,

$$I(\vec{k}', \vec{k}) = \int \psi_{\vec{k}'}{}^*(\vec{r})\psi_{3d}{}^*(\vec{r}')\psi_{3d}(\vec{r})\psi_{\vec{k}}(\vec{r}')$$
$$\times v(\vec{r}-\vec{r}')d\vec{r}d\vec{r}', \qquad (3)$$

where $\psi_{3d}(\vec{r})$ is the localized electron orbital, and $v(\vec{r})$ is the Coulomb interaction. The approximations made by OS in treating this, which are essentially the same as those made in the standard theory,[3] are

$$u_{\vec{k}}(0) = \text{constant, independent of } \vec{k}. \qquad (a)$$

$$I(\vec{k}+\vec{q}, \vec{k}) = F_{3d}(\vec{q}) = \int d\vec{r} \exp(i\vec{q}\cdot\vec{r}) |\psi_{3d}|^2. \qquad (b)$$

$$\epsilon_{\vec{k}} \propto k^2. \qquad (c)$$

Although the "justification" of (b) given by OS is valid if the band orbitals are simply $\propto \exp(i\vec{k}\cdot\vec{r})$, it is not a valid justification in general: Even in the case $v(\vec{r}-\vec{r}') \propto \delta(\vec{r}-\vec{r}')$, $I(\vec{k}+\vec{q}, \vec{k})$ does not reduce to the magnetic form factor F_{3d} [because of the factor $u_{\vec{k}}(\vec{r})u_{\vec{k}+\vec{q}}(\vec{r})$ which also occurs in the integrand of I].

As is well known, these approximations give $\sigma(\vec{q}) = \chi_0(q)F_{3d}(\vec{q})$, where $\chi_0(q)$ is the free-electron spin susceptibility. Furthermore, as pointed out by OS,[1,4] this yields a spin density $S_0(R)$ which, for $R \neq 0$, can give reasonably good agreement with the hyperfine field measurements (see Fig. 2). For this we have used $k_F = 1.2$ Å^{-1}

(in agreement with OS), giving a 4s conduction electron/atom ratio of 0.66. But, as OS point out, $S_0(0)$ is then about a factor of 7 larger than a value which would give consistency with the hyperfine field in pure iron.

Let us first consider (a), leaving (b) and (c) as assumptions. Putting $u_{\vec{k}}(\vec{r})$ = const (independent of $\vec{k}$) is clearly poorest when $\vec{r}$ is inside the atomic core, and so it is for the hyperfine experiment. However, it is only the k dependence of $u_{\vec{k}}(0)$ that is pertinent here, since the discussion is concerned only with the <u>ratios</u> of hyperfine fields at the different R. To get a rough idea as to the effect of (a), we have taken $\psi_{\vec{k}}(\vec{r})$ to be a single plane wave orthogonalized to the core electrons. Neglecting overlap between core electrons on different atoms, this gives $u_{\vec{k}}(0) = A_{\vec{k}}\{1 - \sum_c \psi_c(0) f_c(\vec{k})\}$, where $f_c(\vec{k})$ is the Fourier transform of $\psi_c{}^*$, $A_{\vec{k}}^{-1} = V^{1/2}\{1 - n\sum_c |f_c(\vec{k})|^2\}^{1/2}$, n = number of atoms per unit volume, and the sum is over one core. We then approximated $\psi_c(\vec{r})$ by hydrogenic wave functions, choosing the screening constants to match the location of the outer extremum in $r \times$ (radial function) with that of the Hartree-Fock-Slater function.[5] The only appreciable contribution in $A_{\vec{k}}$ is from the 3s orbital, and $n|f_{3s}(k)|^2$ is only ≈ 0.1, so we take $A_{\vec{k}}^{-1} \cong V^{1/2}$. Then

$$V^{1/2}u_{\vec{k}}(0) = \alpha(k) - 24\left(1 - \frac{10}{3}\frac{k^2}{\beta^2} + \frac{k^4}{\beta^4}\right)\left(1 + \frac{k^2}{\beta^2}\right)^{-4}$$

$$\equiv \alpha(k) - 24g(k), \qquad (4)$$

where $\alpha(k) = 1 - f_{1s}(k)\psi_{1s}(0) - f_{2s}(k)\psi_{2s}(0)$, $24g(k) = f_{3s}(k)\psi_{3s}(0)$. β, the quantity appearing in
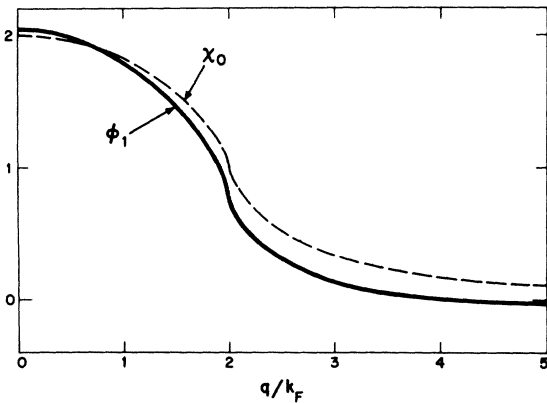

FIG. 1. Approximations to the function $\varphi(\vec{q}) \equiv \sigma(\vec{q})/F_{3d}(\vec{q})$. With assumptions (a), (b), and (c), $\varphi(\vec{q}) = \chi_0(q)$, the free-electron susceptibility. With assumption (a) corrected as described in the text, $\varphi(\vec{q}) = \varphi_1(q)$.

$\exp(-\beta r)$ in ψ_{3s}, is 11.1 Å^{-1} by our criterion, the outer maximum occurring at 0.37 Å; the corresponding β's for the 1s and 2s functions are 45 and 22 Å^{-1}, respectively. The fact that the k variation of the 1s and 2s functions is slow compared to $f_{3s}(k)$ suggests that $\alpha(k)$ may be approximated by a constant. We find indeed that replacing $\alpha(k)$ by 6 in Eq. (4) gives a good approximation, for our present purposes, to the function defined by (4). [Note that $\alpha(0) = 9.$]

Writing $\sigma(q) = \varphi_1(q/k_F)F_{3d}(q)$, $\varphi_1(q/k_F)$ was calculated using (4) in the approximation just described, (2), (b), and (c), taking advantage of $\beta^2/k_F{}^2 \gg 1$ for simplification. The result is shown in Fig. 1. $\varphi_1(Q)$ was normalized so that its singular term, which is of the same form as that in $\chi_0(Q)$, has the same coefficient as that in χ_0. This was done (arbitrarily) so that the two spin densities $S_1(R)$, $S_0(R)$, would be expected to approach each other at sufficiently large R.[6] We see from Fig. 1 that the essential difference between $\varphi_1(Q)$ and $\chi_0(Q)$ is that φ_1 decreases rather more rapidly than χ_0. Remembering that after the angular integration in (1), one has

$$S(R) \propto \int_0^\infty Q^2 \frac{\sin QR}{QR} \varphi(Q) F_{3d}(Q) dQ,$$
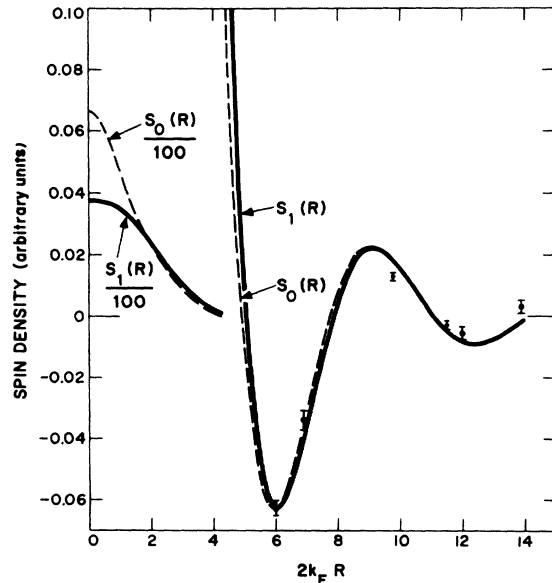

FIG. 2. s-electron spin density as computed from Eq. (1). $S_0(R)$ and $S_1(R)$ correspond to $\varphi = \chi_0$ and $\varphi = \varphi_1$, respectively. Only the values of $S(r)$ at the lattice points $r = R$ are significant. Note the renormalization of $S(R)$ for $2k_F R < 4.25$. The experimental points are from Stearns and Wilson.

the Q^2 factor rendering the small difference between φ_1 and χ_0 at small Q insignificant, hence we expect $S_1(0) < S_0(0)$ and $S_1(R) \sim S_0(R)$ for large R. The integrals dQ were evaluated numerically, and the results are shown in Fig. 2. The expected behavior just outlined is seen to occur. It is interesting that the nearest neighbor distance R_{nn} is already large in the sense that $S_1(R) \cong S_0(R)$ for $R \gtrsim R_{nn}$—this is not too surprising since $2k_F R_{nn} \cong 6$. Thus we see that

$$S_1(R) \cong S_0(R), \quad R \neq 0;$$

$$S_1(0) = S_0(0)/1.8; \tag{5}$$

showing an appreciable reduction in the discrepancy between experiment and a theory neglecting s-s interactions. We estimate that the error in this result as compared to the exact calculation based on (4), (2), (b), and (c) is less than 5% for $S_1(0)$ and negligible for $S_1(R)$ at nonzero R. Also the k dependence of A_k should decrease $S_1(0)$ slightly. The conclusion to here is that $S(0)$ is sensitive and $S(R)$ is insensitive to modifications presumably in the direction of a more realistic approximation[7] to the conduction-electron orbitals ψ_k. In other words, approximation (a) is probably important, particularly with respect to $S(0)$.

A similar conclusion is also warranted for approximation (b): $I(\vec{k}', \vec{k})$ will be determined, roughly speaking, by $u_k(\vec{r})$, where $\vec{r}$ is the location in the maximum of ψ_{3d} ($\vec{r} \cong 0.36$ Å [5]). $\psi_c(\vec{r}) f_c(k)$ is negligible for the $1s$ and $2s$ functions, changing the α in Eq. (5) to 1; and $\psi_{3s}(\vec{r}) \sim \psi_{3s}(0)/16$, reducing the coefficient of $g(k)$ from 24 to ~1.5. The closeness of this latter coefficient to 1 suggests an even greater percent variation with $\vec{k}$ and $\vec{k}'$ than the effect calculated above.[8] However, this calculation is complicated by the $3p$ and $3d$ core functions (particularly). In view of the suggested sensitivity, a more careful calculation should be made. Such a calculation will involve going beyond the simple single orthogonalized plane-wave approximation.

Nevertheless, despite these difficulties, our discussion leads clearly to the conclusion that a large discrepancy between observation and a calculation based on (a) and (b) of $S(0)$ (even a factor of 7) is far from sufficient to throw out the basic theory neglecting s-s interactions.

In our opinion, the small discrepancies in $S(R)$ at large R might be more significant than the relatively large one at $R = 0$, assuming that the experimental limits of error are meaning-

ful. As suggested by Zeiger,[9] they might reflect actual deviations from the free-electron Fermi surface, i.e., deviations from approximation (c).

Finally, we remark briefly about the relation between the spin susceptibility $\chi(\vec{q})$ [the $\vec{q}$th Fourier component in the response to a field $\exp(i\vec{q}\cdot\vec{r})$][10] and the function $\varphi(\vec{q}) = \sigma(\vec{q})/F_{3d}(\vec{q})$. First of all, the spin density arising from exchange can only approximately be described in terms of the response to a local potential $\mathcal{K}(\vec{r})$—it would be exact if $v(\vec{r}) \propto \delta(\vec{r})$ in the band-local exchange matrix element and $\mathcal{K}(\vec{r}) \propto \psi_{3d}(\vec{r})^2$. Even with this approximation, the identification[1] of $\varphi(\vec{q})$ with $\chi(\vec{q})$ is incorrect; the correct relation can be shown to be $\varphi(\vec{q}) = \sum_{\vec{K}} \chi(\vec{q} + \vec{K}, \vec{q})$, where $\chi(\vec{q}', \vec{q})$ is the $\vec{q}'$ response to a field $\exp(i\vec{q}\cdot\vec{r})$ and $\vec{K} = 2\pi \times$(reciprocal vector). Of course, $\chi(\vec{q}) = \chi(\vec{q}, \vec{q})$. In a gas (no periodic potential), $\chi(\vec{q}', \vec{q})$ is diagonal. Hence, before a knowledge of the qualitative behavior of $\chi_{gas}(\vec{q}, \vec{q})$ can be transferred to $\varphi(\vec{q})$, further analysis is necessary.

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[6]See T. A. Kaplan and D. H. Lyons, Phys. Rev. **129**, 2072 (1963), Appendix 2. The essential intuitive idea is that for very large R, the rapid oscillations in $\exp(i\vec{q}\cdot\vec{R})$ as a function of q cause cancellation over most of the integrand in (1), the main contribution coming from near $q = 2k_F$, where $\partial\varphi(q)/\partial q \to -\infty$.

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[8]A very crude idea of this can be obtained, simply, by taking $\alpha = 16$ (so $24/\alpha = 1.5$) in Eq. (4) and formally maintaining approximations (b) and (c). This gives a $\varphi(Q)$ which is even more rapidly decreasing than $\varphi_1(Q)$; $S(0)$ becomes negative with $S_0(0)/S(0) \cong -3$; and $S(R)$ is slightly modified for $R \neq 0$, requiring a few percent increase in k_F to obtain the same quality fit to the experimental points. Comparison of this result with OS emphasizes the fact that knowledge of $S(\vec{R})$ only at the lattice points does not determine the integrand of Eq. (1).

[9]H. J. Zeiger, private communication.

[10]The spin susceptibility is defined in terms of the response to a driving term in the Hamiltonian of the form $-\sum_i \mathcal{K}(\vec{r}_i) s_{iz}$, where $\mathcal{K}(\vec{r})$ is the applied "field," $\vec{r}_i$, s_{iz} are the position and spin of the ith electron, respectively.