tion potentials obtained from piezobirefringence and those calculated with the simple model that attributes the deformation potentials to the effect of the Madelung potential in the anisotropic "*p*" wave function of the valence band of the stressed crystal[2] is not surprising.

The authors would like to thank Dr. M. Cardona for many helpful discussions.

[†]Present address: Superior Electronics, Inc., Montreal 331, Quebec, Canada.

*Work supported in part by the National Research Council of Canada.

[1] U. Gerhardt and E. Mohler, Phys. Status Solidi 18, K45 (1966).

[2] A. Gavini and M. Cardona, Phys. Rev. 177, 1351 (1969).

[3] Clevite Corp., Piezoelectric Division, Bedford, Ohio.

[4] M. Cardona, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1969), Suppl. 11.

[5] See Ref. 2, p. 1352.

[6] C. W. Higginbotham, M. Cardona, and F. H. Pollack, Phys. Rev. 184, 821 (1969).

[7] P. Yu, M. Cardona, and F. H. Pollak, Bull. Am. Phys. Soc. 15, 754 (1970).

[8] U. Gerhardt, D. Beaglehole, and R. Sandrock, Phys. Rev. Letters 19, 309 (1967).

[9] A. Gavini and M. Cardona, Phys. Rev. 1, 672 (1970).

[10] J. C. Hensel and K. Sukuzi, Bull. Am. Phys. Soc. 14, 113 (1969).

[11] L. D. Laude, F. H. Pollak, and M. Cardona, Bull. Am. Phys. Soc. 15, 289 (1970).

PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Pseudopotential Calculation of the Knight Shift and Relaxation Time in Magnesium

P. Jena* and T. P. Das*
Department of Physics, University of Utah, Salt Lake City, Utah 84112

and

S. D. Mahanti
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 21 January 1970)

A nonlocal pseudopotential procedure has been utilized to obtain the conduction electron wave functions in magnesium metal. It is found that the use of these wave functions along with a finer scanning of the Fermi surface, namely, 110 points in $\frac{1}{24}$ of the Brillouin zone, leads to a value for the Knight shift K_s in much better agreement with experiment than was an earlier value obtained by the orthogonalized-plane-wave procedure. Possible sources for the difference in theoretical K_s values obtained by using these two different procedures are discussed. Improved values of the relaxation time T_1 and Korringa constant are also presented.

In a recent paper[1] we have analyzed the Knight shift (K_s) and nuclear spin-lattice relaxation time (T_1) in magnesium using wave functions obtained from orthogonalized-plane-wave (OPW) calculations. These calculations incorporated the effects of exchange core polarization[2] (ECP) and the exchange enhancement of spin susceptibility (χ_s) through currently available procedures.[3] The theoretical value of the Knight shift was[1] found to be 0.056% as compared to the experimental value[4,5] of 0.112%. In a search for possible sources for improving the agreement between experiment and theory, we have reevaluated the conduction electron spin density $\langle|\Psi_{\vec{k}_F}(0)|^2\rangle_{\text{av}}$ using wave functions derived from available[6] nonlocal pseudopotential band calculations in this metal. In addition to the usefulness of such an analysis in explaining hyperfine properties of magnesium, the results are also useful in explaining the relationship between wave functions obtained by direct OPW calculations and through the use of pseudopotentials. Such a comparison is important in view of the increasing use that is being made currently of pseudopotentials and model potentials, not only for investigation of properties depending on the band structure, but also of hyperfine properties depending on wave functions. No such comparison is currently available for the hyperfine properties in any one metal. Magnesium[6,7] and indium[8,9] are the only two metals where such a comparison is currently possible due to the availability of both types of band calculations.

The nonlocal pseudopotential parameters utilized were those recently obtained by Kimball *et al.*[6] from an analysis of detail Fermi-surface data of magnesium. The Fermi-surface dimensions derived from this pseudopotential were found to be in very good agreement with experimental dimensions. Wave functions were calculated at 110 points on the Fermi surface (FS) in $\frac{1}{24}$ of the Brillouin zone (BZ) and provided a fairly detailed scanning of the major segments of the FS, namely, lens, cigar, butterfly, and monster. The linear combinations of the plane waves derived from the pseudopotentials were converted into a linear combination of OPW functions by orthogonalization to atomic 1*s*, 2*s*, and 2*p* core functions. The average over each segment was carried out by the usual[1] weighting process involving the local density of states, namely,

$$\langle |\Psi_{\vec{k}_F}(0)|^2\rangle_j = \sum_i |\Psi_{\vec{k}_F}(0)|^2_{ij} g_{ij}(\vec{k}_F) / \sum_i g_{ij}(\vec{k}_F), \tag{1}$$

where j refers to a particular segment of the Fermi surface and i corresponds to the ith point in that segment. $g_{ij}(\vec{k}_F)$ defines the local density of states of the point denoted by indices ij and is given by

$$g_{ij}(\vec{k}_F) = |\nabla_{\vec{k}_F} E|_{ij}^{-1} . \tag{2}$$

The spin densities, normalized over the Wigner-Seitz volume, from various segments of the FS are listed in Table I and compared with earlier values[1] obtained through the OPW procedure. For a detailed description of the variation of the spin density over two important segments, the lens and the monster, we have presented the spin densities[10] for points on the lens in the Γ*AHK* cross section in Fig. 1 and those on the monster in Γ*KM* cross section in Fig. 2. From Table I and Figs. 1 and 2, major changes in the spin density between pseudopotential and OPW procedures appear to occur for the lens, cigar, and monster. For all these three segments, there is a sharp increase in the spin density with the most marked change occurring in the monster. For the butterfly, on the other hand, there is a slight decrease in the spin density.

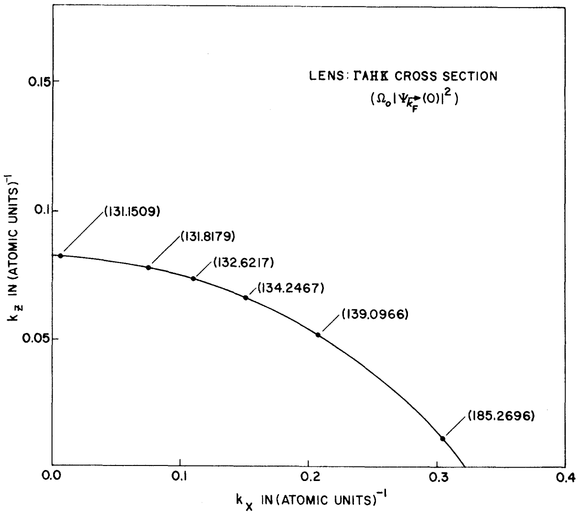

FIG. 1. Direct spin density contribution from individual points on the Γ*AHK* cross section of "lens."

There are two ways in which the spin density can differ for the two calculations, namely, through the radial characters of the core wave functions used in the construction of OPW functions in the two cases[7,11] or through a change in the mixing of $\vec{k}$ and $(\vec{k}+\vec{K})$ states brought about by the potential. The effect of the first is less pronounced because the major effect on the spin density arises through the terms $b_{ns}(\vec{k})\, b'_{ns}(\vec{k})\, \Psi_{ns}(0)\, \Psi'_{ns}(0)$, where the overlap integrals (orthogonalization parameters) $b_{nl}(\vec{k})$ are defined by

$$b_{nl}(\vec{k}) = \langle e^{i\vec{k}\cdot\vec{r}} | \Psi_{nl}(\vec{r})\rangle . \tag{3}$$

In Eq. (3), $\Psi_{nl}(\vec{r})$ refers to the atomic core function. While the pseudocores used in the OPW procedure give smaller $\Psi_{ns}(0)$ than the real cores used here, the former provide a compensating increase in the spin density through $b_{ns}(\vec{k})$, since the overlap is larger for the extended pseudocore functions. It thus appears that the major change occurs through differences in mixing of $\vec{k}$ and $\vec{k}+\vec{K}$ states in the two cases. Over most of the FS, there appears to be a larger mixing of $\vec{k}$ and $\vec{k}+\vec{K}$

TABLE I. Pseudopotential and OPW results of the direct spin density in magnesium from various segments of the FS. The conduction electron wave function is normalized over the Wigner-Seitz volume Ω_0.

		Spin density in units of $1/\Omega_0$		Average direct spin density in units of $1/\Omega_0$	
Segment of FS	Surface area in a.u.	Pseudo-potential	OPW	Pseudo-potential	OPW
Lens	0.6366	0.9341	0.6377	0.5875	0.2409
Cigars	0.6252	0.4256	0.0813		
Butterflies	1.3452	0.5961	0.7050		
Monster	3.9996	0.5547	0.0466		

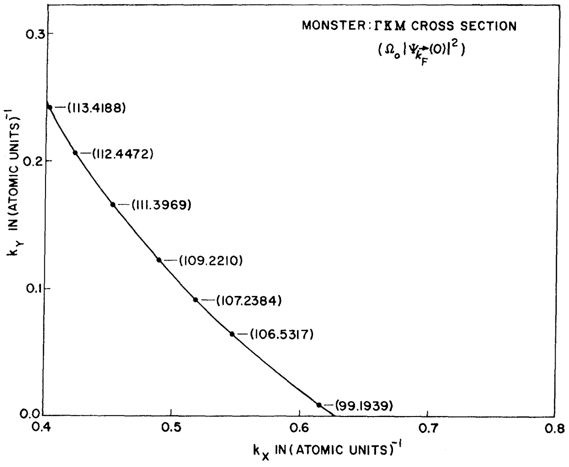

FIG. 2. Direct spin density contribution from individual points on the ΓKM cross section of "monster."

states for the OPW calculation and subsequent increase in the p character.

The exchange core polarization[1,2] (ECP) contribution to the Knight shift was calculated using the moment perturbation (MP) procedure[12] as in Ref. 1 and leads to the results

$$K_s^{\mathrm{CP},s}(\mathrm{PP})/K_s^{\mathrm{CP},s}(\mathrm{OPW}) = 2.44\ , \tag{4}$$

and

$$K_s^{\mathrm{CP},p}(\mathrm{PP})/K_s^{\mathrm{CP},p}(\mathrm{OPW}) = 0.64\ , \tag{5}$$

where $K_s^{\mathrm{CP},s}$ and $K_s^{\mathrm{CP},p}$ are, respectively, the s and p parts of the ECP contributions to the Knight shift.

The notations PP and OPW refer to the values obtained from pseudopotential and OPW calculations, respectively. The changes in the d part of the ECP contribution to Knight shift $K_s^{\mathrm{CP},d}$ are unimportant because $K_s^{\mathrm{CP},d}$ itself is very small. The increase in $K_s^{\mathrm{CP},s}$ and decrease in $K_s^{\mathrm{CP},p}$ reflect the increase in the s character and corresponding decrease in the p character in going from OPW to pseudopotential calculations. However, since $K_s^{\mathrm{CP},s}$ and $K_s^{\mathrm{CP},p}$ are positive, the change in the total ECP contribution to Knight shift K_s^{CP} is less marked, namely,

$$K_s^{\mathrm{CP}}(\mathrm{PP})/K_s^{\mathrm{CP}}(\mathrm{OPW}) = 1.63\ , \tag{6}$$

as compared to the ratio of the direct contributions to the Knight shift K_s^d,

$$K_s^d(\mathrm{PP})/K_s^d(\mathrm{OPW}) = 2.44\ . \tag{7}$$

Our theoretical value of the total Knight shift derived from the pseudopotential procedure is

$$K_s = 0.12\%\ , \tag{8}$$

where we have used χ_s obtained in Ref. 1. The theoretical value of K_s in Eq. (8) is in much better agreement with experimental value (0.112%) than the earlier OPW results (0.056%).

The good agreement with experiment thus indicates that the importance of the combined effect of other mechanisms such as orbital and conduction-conduction polarization mechanisms is much less important than was anticipated in Ref. 1. However, it is worthwhile to investigate the individual importance of these mechanisms separately. As regards the comparison between the results from pseudopotential and OPW calculations, it is disappointing that there are sizable differences. One does not have any clear-cut reasons for preferring one value over the other as being more accurate because the OPW calculation has the advantage of being first principle in character while the pseudopotential has the merit of being obtained from the experimental data. It is, however, not unreasonable to consider the better fit that the band structure obtained from the pseudopotential gives with the de Haas-van Alphen data, and the better agreement with experimental Knight shift data as evidence for the correctness of the pseudopotential utilized. One is then left with the problem of finding the reasons for possible errors in the OPW result. In the case of the OPW model, the potential was of course calculated from first principles, and therefore the only criticism that can be leveled against it is the lack of self-consistency. Perhaps a more important difficulty with the OPW calculation is the use of the more diffuse pseudo-core-functions which perhaps lead to appreciable overlap between neighboring ion sites. The neglect of these overlaps could produce possible errors in the matrix elements of the potential and thereby influence the linear combinations of the OPW's which determine the relative amounts of s and p character. It thus appears that it would be helpful to recalculate the energy bands and hyperfine properties of magnesium for the OPW formulation making use of both real core functions and self-consistent potential in order to improve our understanding of the conduction-electron wave functions obtained by the procedures. Similar comparisons between these two models in other metals would also be desirable.

Lastly, we can predict the relaxation rate in magnesium using the spin density from our pseudopotential calculations. The effects of core polarization on relaxation time T_1 are incorporated through the expression

$$\left(\frac{1}{T_1T}\right) = \left(\frac{1}{T_1T}\right)_{d+CP,s} + \frac{1}{3}\left(\frac{1}{T_1T}\right)_{CP,p} + \frac{1}{5}\left(\frac{1}{T_1T}\right)_{CP,d} + \cdots\ , \tag{9}$$

where the suffixes have the same meaning as in earlier work.[1] It should be remarked, however, that Eq. (9) holds rigorously only for a spherical FS which is equivalent to using a one-OPW approximation.[13] One expects departures from it even in the presence of cubic distortions which can split the d bands. For noncubic symmetry, the p bands also split, and appropriate corrections have to be introduced in the degeneracy factors $2l+1=3, 5, \ldots$ in Eq. (9). In magnesium, the core-polarization contributions from non-s components of the wave function are quite small and therefore the crystal-field corrections to Eq. (9) do not influence the results significantly.

An additional consideration in evaluating relaxation times is the question of the role of exchange enhancement. If one uses the band density of states in the expression for T_1,[1,14] this would correspond to neglecting enhancement effects completely. Actually one has to incorporate enhancement effects as in the case of K_s. In this connection, the relevant spin susceptibility function for T_1 is wave-number dependent because the field of the nucleus is nonuniform. The theory for this effect was first worked out by Moriya[15] for free electrons. However, an appropriate adaptation to band electrons can be made as in an earlier work.[1] The procedure for this is to adjust Moriya's free-electron result[15] to make $\chi(\vec{q})$ match the exchange enhanced result for the uniform field susceptibility $\chi(0)$ in the effective mass approximation.[3]

Using our calculated spin densities from direct and $s, p,$ and d parts of the ECP contribution, and the band density of states the unenhanced results for T_1T are given by

$$(T_1T)^{-1}_{d+\text{CP},s} = 10.94\times10^{-3}\,\text{deg sec}\,, \tag{10}$$

$$(T_1T)^{-1}_{\text{CP},p} = 0.02\times10^{-3}\,\text{deg sec}\,, \tag{11}$$

and
$$(T_1T)^{-1}_{\text{tot}} = 10.94\times10^{-3}\,\text{deg sec}\,; \tag{12}$$

thus,
$$(T_1T)^{\text{unenhanced}}_{\text{tot}} = 91.74\,\text{deg sec}. \tag{13}$$

On introducing exchange-enhancement effects in the manner indicated,[1]

$$(T_1T)^{\text{enhanced}}_{\text{tot}} = 58.91\,\text{deg sec}. \tag{14}$$

This leads to a predicted relaxation time T_1,

$$T_1 = 14.03\,\text{sec} \quad \text{at } 4.2\,^\circ\text{K}. \tag{15}$$

Unfortunately, no experimental value of the relaxation time in magnesium is available at present to compare with the predicted relaxation rate except for the observation[5] of appreciable saturation at 1.2 °K indicating that T_1 is reasonably long and in qualitative agreement with Eq. (15). Finally, the theoretical Korringa ratio,

$$R = (K_s^2T_1T)^{\text{theor}}/(K_s^2T_1T)_{\text{ideal}}\,, \tag{16}$$

is found to be

$$R^{\text{theor}} = 1.23, \tag{17}$$

indicating that a 23% departure is expected from the value for noninteracting free electrons for which R is unity.

---

*The portion of this investigation carried out at the University of Utah, Salt Lake City, Utah 84112 was supported by the National Science Foundation.

[1] P. Jena, T. P. Das, and S. D. Mahanti, Phys. Rev. B 1, 432 (1970).

[2] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) 73, 811 (1959).

[3] S. D. Silverstein, Phys. Rev. 130, 912 (1963).

[4] T. J. Rowland, in *Progress in Material Science*, edited by Bruce Chalmers (Pergamon, New York, 1961), Vol. IX, p. 14.

[5] P. D. Dougan, S. N. Sharma, and D. L. Williams, Can. J. Phys. 47, 1047 (1969).

[6] J. C. Kimball, R. W. Stark, and F. M. Mueller, Phys. Rev. 162, 600 (1967).

[7] L. M. Falicov, Phil. Trans. Roy. Soc. London A225, 55 (1962).

[8] N. W. Ashcroft and W. E. Lawrence, Phys. Rev. 175, 938 (1968).

[9] G. D. Gaspari and T. P. Das, Phys. Rev. 167, 660 (1968).

[10] The spin densities listed in Table I are quoted up to the fourth decimal place. However, the Knight shifts and relaxation times in the rest of the paper are given up to the second decimal place since the static and dynamic susceptibilities utilized in deriving them are only approximate.

[11] To be consistent with the choice utilized by Kimball *et al.* (Ref. 6) in deriving the pseudopotential parameters, we have used atomic Hartree-Fock-Slater core wave functions [(see F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, New York, 1965)], in the evaluation of the orthogonalization parameters $b_{nl}(\vec{k})$ (Eq. 3). However, in evaluating $\Psi_{ns}(0)$ for core functions, we have used Hartree-Fock wave functions obtained by J. B. Mann [LASL Report, 1968 (unpublished)].

[12] G. D. Gaspari, W. M. Shyu, and T. P. Das, Phys. Rev. 134, A852 (1964).

[13] S. D. Mahanti, L. Tterlikkis, and T. P. Das, in *Proceedings of the International Symposium on Electron and Nuclear Magnetic Resonance, Australia*, 1969 (Plenum, New York, 1970), p. 91.

[14] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

[15] T. Moriya, J. Phys. Soc. Japan 18, 516 (1963).