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Shape dependence of the conduction-electron spin-resonance g shift in a small sodium particle

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A previous calculation of the size dependence of the conduction-electron spin-resonance g shift for a small particle of sodium with cubic shape is extended to the case of a particle with spherical shape. Within a model where the conduction-electron wave functions are approximated by single orthogonalized standing waves, it is found that one of the major size-dependent contributions to the g shift displays, for a spherical particle, the same qualitative size dependence as was obtained previously for a cubic particle. Specifically, we find that this term can be written as $\delta g(R) = [1-\beta(a/R)]\delta g(\infty)$, where a is the lattice constant, β is a parameter of the order of unity, R is the radius of the spherical particle, and $\delta g(\infty)$ is the bulk g shift.

I. INTRODUCTION

In previous papers[1,2] (Ref. 2 will henceforth be referred to as I) we have proposed and developed an orthogonalized-standing-wave (OSW) method for calculating the conduction-electron wave functions in small particles of simple metals. Furthermore, we have applied this method to make a detailed study of the size dependence of the conduction-electron spin-resonance (CESR) g shift in a small particle of sodium. Our motivation for this study was that the only other existing theory of the size dependence of the CESR g shift, developed by Kawabata,[3] is in disagreement both with recent experiments,[4] and with a one-dimensional model calculation.[5]

The OSW method is a finite-size generalization of the standard orthogonalized-plane-wave (OPW) method,[6–8] wherein the conduction-electron wave functions are modeled as standing waves in a finite volume which are orthogonalized to all core states of the metallic atom. In our previous work[1,2] we have assumed that the finite volume in which the conduction electrons are confined is a cubic box of edge length L. Thus, our previous calculations of the size dependence of the CESR g shift in both the single[1,2] and multiple[2] OSW approximations are strictly valid only for a small cubic shaped particle of sodium. We have, however, made the assertion[1,2] that our results for the size dependence of the g shift do not depend strongly on the restriction to that shape.

It is the purpose of the present Brief Report to present the results of a calculation of one of the major contributions to the CESR g shift, within the single OSW approximation, for a *spherical* particle of sodium and to thus confirm this assertion. Measurements of the g shift and other CESR line-shape properties in small metallic particles as functions of particle size are of considerable interest to a number of experimental groups[4,9–22] and the experimentally prepared particles are neither cubic nor truly spherical in shape. Thus knowledge that the size dependence of these quantities is essentially independent of particle shape should be useful for experimental-theoretical comparisons.

II. REVIEW OF RESULTS FOR A SODIUM CUBE

In I, we have shown that the term denoted as δg^P (Refs. 8 and 23–30) is one of the dominant size-dependent contributions to the g shift in sodium. We have found that,[2] for a sodium cube of edge length L, this term can be written in the single OSW approximation as

$$\delta g^P(L) = \frac{48\pi}{a_{\rm sc}^3}\left(1-\frac{2a_{\rm sc}}{L}\right) J_P(\gamma_F) J_\Delta(\gamma_F) \frac{\langle \gamma_{xF}^2+\gamma_{yF}^2\rangle}{\gamma_F^2} , \tag{1a}$$

where $a_{\rm sc}^3$ is the unit cell volume, $\vec{\gamma}_F$ is the Fermi wave vector of the small particle (which, in general, can depend on size and is not necessarily equal to the bulk Fermi wave vector $\vec{k}_F$), γ_{xF}, γ_{yF}, and γ_F are its x and y components and magnitude, the angular brackets denote an average over the Fermi surface, and $a_{\rm sc}$ is the effective simple cubic lattice constant for sodium.[2] The latter quantity is defined as $a_{\rm sc} = a/(2)^{1/3}$, where a is the true bcc lattice constant. In Eq. (1a), we have defined the functions

$$J_p(\gamma_F) = [J_{1/2}(\gamma_F) + 2J_{3/2}(\gamma_F)]/3 , \tag{1b}$$

and

$$J_\Delta(\gamma_F) = [J_{1/2}(\gamma_F) - J_{3/2}(\gamma_F)]/3 , \tag{1c}$$

in which

$$J_\alpha(\gamma_F) = \int_0^\infty R_\alpha(r) j_1(\gamma_F r) r^2\, dr . \tag{1d}$$

Here the functions $R_\alpha(r)$ are the radial parts of the wave functions for the $2p_{1/2}(\alpha=\frac{1}{2})$ and $2p_{3/2}(\alpha=\frac{3}{2})$ core states of sodium, and $j_1(\gamma_F r)$ is a spherical Bessel function of order 1. The functions $R_\alpha(r)$ have been calculated and displayed in parametrized form by DeGraaf and Overhauser.[8]

As is discussed in I, in the calculation of δg^P, which leads to the result shown in Eq. (1), the relationship

$$L=(N+1)a_{\mathrm{sc}} \tag{2}$$

has been assumed, where N is the number of atoms along a cube edge and a simple cubic lattice has been assumed. As is shown in detail in I, altering this relationship or choosing the correct, but calculationally more difficult, bcc lattice for the sodium particle will serve only to slightly change the multiplicative factor in front of the size-dependent correction a_{sc}/L in Eq. (1). The calculations of I also have been shown that the Fermi surface has only a weak size dependence which can, for all but the very smallest particles, be neglected in comparison with the size-dependent prefactor in Eq. (1).

We thus conclude in I that the size dependence of δg^P for a sodium cube may be written approximately as

$$\delta g^P(L) \simeq \left(1-\frac{\alpha a}{L}\right) g^P(\infty) , \tag{3}$$

where α is a parameter of the order of unity and $\delta g^P(\infty)$ is the bulk value of δg^P. Furthermore, we have shown in I that this form is unchanged if a more accurate multiple OSW calculation[2] is performed. It should also be noted that the size dependence predicted by Eq. (3) is expected to be qualitatively correct for particles other than sodium and that it is in qualitative agreement with the size dependence of the g shift observed by Millet and Borel[4] for small magnesium particles.

III. OUTLINE OF SINGLE OSW THEORY FOR A SPHERICAL PARTICLE OF SODIUM

While the calculational details of the OSW method are different for cubic and spherical shaped particles, essentially all of the general formalism is identical for the two cases. Thus only a brief outline of the theory will be given here and the reader is referred to I for more details. Furthermore, since the results of I show clearly that the multiple OSW approximation results for the size dependence of the g shift are qualitatively similar to the single OSW results, and since the multiple OSW calculations require a large amount of computation, while the single OSW calculations can be done essentially analytically, only the single OSW approximation will be discussed here.

Following I, we assume, in the spirit of the frozen core approximation, that the core states are unchanged in the cluster from those in the infinite crystal. We can thus describe these states in the same parametrized form and with the same values of the parameters as DeGraaf and Overhauser[8] have done for their bulk sodium wave functions. Also following I, in order to simulate the effect of the potential barrier at the surface of the spherical particle of radius R, we assume an infinite potential barrier at the surface.

In the single OSW approximation, the spin-up conduction electron wave function for a spherical particle of sodium is written as

$$\psi_{\uparrow m}(k_{ln},\vec{r})=B_{\uparrow m}(k_{ln})\left(S_m(k_{ln},\vec{r})\binom{1}{0}-\sum_{j,\alpha}\beta^{\alpha}_{\uparrow m}(\vec{R}_j,k_{ln})\,U_\alpha(\vec{r}-\vec{R}_j)\right) , \tag{4}$$

where the arrow indicates spin up, $S_m(k_{ln},\vec{r})$ is a free-electron standing wave normalized to unity in the volume $V=4\pi R^3/3$ of the sphere, the $U_\alpha(\vec{r})$ are the atomic core state wave functions for sodium as calculated by DeGraaf and Overhauser,[8] and α labels the core states. The standing wave has the form

$$S_m(k_{ln},\vec{r})=\left(\frac{2}{R^3}\right)^{1/2}\frac{j_l(k_{ln}r)\,Y_{lm}(\theta,\phi)}{|j_{l+1}(k_{ln}R)|} , \tag{5}$$

where j_l is a spherical Bessel function of order l, Y_{lm} is a spherical harmonic, l is a positive integer, and m is an integer in the range $l\leqslant m\leqslant l$. In Eqs. (4) and (5), k_{ln} is a quantity which plays the role in the small particle that the wave vector does in the bulk. It has the value

$$k_{ln}=x_{ln}/R \tag{6}$$

where x_{ln} is the nth root of the lth spherical Bessel function. In Eq. (4) the orthogonalization coefficients $\beta^{\alpha}_{\uparrow m}(\vec{R}_j,k_{ln})$ are equal to

$$\beta^{\alpha}_{\uparrow m}(\vec{R}_j,k_{ln})=\int_v U^*_\alpha(\vec{r}-\vec{R}_j)\,S_m(k_{ln}r)\binom{1}{0}d^3r , \tag{7}$$

the sum over lattice sites $\vec{R}_j$ goes over the finite number of atoms in the cluster and $B_{\uparrow m}(k_{ln})$ is a normalization coefficient, approximately equal to unity. We shall set it equal to one in what follows, since it does not significantly affect the results of our calculations.

In order to establish a connection between the radius R of the spherical particle and the number of atoms in the cluster, we first assume that the lattice parameter in the small particle is unchanged from its bulk value.[31] For further simplicity we assume, following I, that the particle has a simple cubic lattice structure with the same average density as the body-centered cubic structure found experimentally for bulk sodium.[32] This means that we choose the lattice parameter $a_{\rm sc}$ of the sc structure as[2]

$$a_{\rm sc}=a/(2)^{1/3}\ , \tag{8}$$

where a is the bcc lattice parameter (we use $a=7.984$ a.u. in all of our calculations). Finally, we assume the (admittedly somewhat arbitrary) relationship

$$R=\sqrt{3}(N+1)a_{\rm sc}/2\ , \tag{9}$$

where N is the number of atoms along a cube edge. [A sphere of this radius will entirely enclose a cube of edge length L, where L is given by Eq. (2).] It is shown in I, and we have reverified in the present calculation, that the precise choice of relationship between a linear dimension of the conduction-electron container and the number of atoms along a cube edge does not appreciably affect the results for the g shift.

IV. RESULTS FOR THE g SHIFT OF A SPHERICAL SODIUM PARTICLE: CONCLUSIONS

The formalism for the calculation of the g shift in bulk materials is complicated and has been discussed by a number of authors.[8,23–30] We have also briefly reviewed it in I. Furthermore, although this formalism was developed for bulk crystals, we use it here, following I, to calculate the g shift in a small particle while realizing that the ideal formalism to use would be one designed specifically for finite crystals. Unfortunately, such a formalism does not, at present, exist.

Since we have shown in I that one of the major size-dependent contributions to the g shift is the term in the bulk formalism denoted as δg^P,[8,23–30] we will calculate only this contribution here. The formal expression for this quantity, evaluated at wave vector $\vec{k}$ is[8]

$$\delta g^P(\vec{k})=\frac{2}{\hbar}\int d^3r\,\psi_\uparrow(\vec{k},\vec{r})L_z\psi_\uparrow(\vec{k},\vec{r})\ , \tag{10}$$

where $\psi_\uparrow(\vec{k},\vec{r})$ is the predominantly spin-up conduction-electron wave function for that wave vector, which for the small particle we take to be given by Eqs. (4)–(7) and L_z is the orbital angular momentum operator.

Since CESR experiments measure only the Fermi-surface average of the g shift, $\delta g^P(\vec{k})$ must be evaluated at the Fermi wave vector k_{ln}^F of the small particle and averaged over all integer values of l and n on the Fermi surface. Combining Eqs. (4)–(9), putting the result in Eq. (10), evaluating the result to lowest order in the spin-orbit coupling,[8] and averaging over the Fermi surface, leads, after a considerable amount of algebra, to the expression

$$\delta g^P(R)=\frac{48\pi}{a_{\rm sc}^3}\left(1-\frac{\sqrt{3}a_{\rm sc}}{R}\right)\langle J_p(k_{ln}^F)J_\Delta(k_{ln}^F)\sin^2\theta_F\rangle\ , \tag{11}$$

where the functions J_p and J_Δ are defined in Eqs. (1), θ_F is the angle that the Fermi wave vector makes with the Z axis, and the angular brackets denote an average over the Fermi surface. (That is, over all values of the index n which lead to a k_{ln}^F of the same modulus.) As is shown in Eq. (11), only the spherical Bessel functions in Eq. (4) with $l=1$ contribute to the g shift. This is understandable from the form of the coefficients $\beta_{lm}^\alpha(\vec{R}_j,k_{ln})$ [Eq. (7)] and the fact that only the core p states contribute to δg^P.[8] Furthermore, as is reasonable, the g shift δg^P is completely independent of the index m.

Comparison of Eq. (11), the single OSW expression for the contribution δg^P in a spherical sodium particle and Eq. (1), the result for the same quantity in the same approximation for a cubic particle of sodium, shows that the predicted size dependence is qualitatively the same in both cases. In fact, Eq. (11) can be obtained from Eq. (1) by the replacements $L\rightarrow 2R/\sqrt{3}$, $\gamma_F\rightarrow k_{ln}^F$, and $(\gamma_{xF}^2+\gamma_{yF}^2)/\gamma_F^2\rightarrow\sin^2\theta_F$.

Although the Fermi wave vector and Fermi-surface average have minor size dependences, the dominant size dependence of Eq. (11) lies in the factor $(1-\sqrt{3}a_{\rm sc}/R)$. Furthermore, as in I, we have verified that varying the relationship between R and N, Eq. (9), only changes the multiplicative factor in front of the quantity $a_{\rm sc}/R$ and leaves the functional form of Eq. (11) unchanged. Thus, to a good approximation, Eq. (11) can be rewritten as

$$\delta g^P(R)\simeq(1-\beta a/R)\delta g^P(\infty)\ , \tag{12}$$

where β is a parameter of the order of unity and $\delta g^P(\infty)$ is the bulk value of δg^P.

Clearly, this result is merely the generalization of Eq. (3) to the case of a sphere. Since we have shown in I that Eq. (3) holds in the multiple OSW approximation and that δg^P is one of the dominant terms in the g shift for a cubic particle, it is a reasonable assumption that similar conclusions also hold for the spherical particle result, Eq. (12). Thus the size dependence of the CESR g shift for a small sodium particle should be qualitatively independent of the shape of the particle.

The results found in I for the size dependence of the CESR g shift for a cubic shaped sodium particle [summarized for δg^P in the present paper in Eqs. (1)

and (3)] and the results obtained here for the size dependence of δg^P for a spherical particle of sodium, are both in qualitative disagreement with Kawabata's[3] prediction that the CESR *g* shift should increase with particle size as the square of an average linear dimension. Since our model for the conduction-electron wave functions in a small particle and Kawabata's[3] model (see I for a review of Kawabata's theory) are very different, it is difficult to make an accurate assessment as to which theory is correct. However, it does appear from the results obtained here and in I that Kawabata's[3] theory is incomplete. It should thus be used with caution by experimentalists interpreting data.

In summary, the major conclusions of this work are that (i) within the single OSW approximation, the size dependence obtained for the CESR *g* shift of a small sodium particle is essentially independent of the shape assumed for the particle; (ii) this result is expected to carry over if one performs a more accurate multiple OSW approximation; (iii) the single OSW approximation, while not expected to be quantitatively accurate, is useful for obtaining a qualitative picture of the conduction-electron wave functions in small metal clusters and therefore is useful for obtaining a qualitative functional dependence of experimentally measurable quantities on particle size; and (iv) Kawabata's theory of the *g* shift is not complete and must be applied to the interpretation of experimental data with caution. It is furthermore reasonable to speculate that conclusion (i) should also hold for other measurable quantities.

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[1] C. W. Myles, J. Buttet, and R. Car, Solid State Commun. 30, 325 (1979).

[2] J. Buttet, R. Car, and C. W. Myles, Phys. Rev. B 26, 2414 (1982) (this issue).

[3] A. Kawabata, J. Phys. Soc. Jpn. 29, 902 (1970).

[4] J. L. Millet, doctoral dissertation (Ecole Polytechnique Federale, Lausanne, Switzerland, 1980) (unpublished); J. L. Millet and J. P. Borel (unpublished).

[5] C. W. Myles and J. Buttet, J. Phys. (Paris) 38, C2-133 (1977).

[6] See, for example, R. N. Euwema, D. J. Stukel, and T. C. Collins, in *Computational Methods in Band Theory,* edited by A. M. Marcus *et al.* (Plenum, New York, 1971).

[7] For an early application of the OPW method to the band structure of sodium, see H. Schlosser and P. M. Marcus, Phys. Rev. 131, 2529 (1963).

[8] The application of the OPW method to the calculation of the *g* shift in bulk sodium was done by A. M. DeGraaf and A. W. Overhauser, Phys. Rev. B 2, 1437 (1970).

[9] See, for example, J. P. Borel and J. L. Millet, J. Phys. (Paris) 38, C2-115 (1977), and Refs. 10–22.

[10] A. Berhault, S. Bederf, and J. Matruon, J. Phys. Chem. Solids 38, 913 (1977).

[11] D. M. Lindsay, D. R. Herschback, and A. L. Kwiram, Mol. Phys. 32, 1199 (1976).

[12] M. A. Smithard, Solid State Commun. 14, 411 (1974).

[13] D. A. Gordon, Phys. Rev. B 13, 3738 (1976).

[14] G. A. Thompson and D. M. Lindsay, J. Chem. Phys. 74, 959 (1981).

[15] R. C. McMillan, J. Phys. Chem. Solids 25, 773 (1964).

[16] J. L. Millet and R. Monot, in *Proceedings of the Eighteenth Colloque Ampère on Magnetic Resonance and Related Phenomena, Nottingham, England, 1974,* edited by P. S. Allen, E. R. Andrew, and C. A. Bates (North-Holland, Amsterdam, 1975), p. 319.

[17] S. C. Jain, N. D. Arova, and T. R. Reddy, Phys. Lett. 54A, 53 (1975).

[18] A. Chatelain, J. L. Millet, and R. Monot, J. Appl. Phys. 47, 3760 (1976).

[19] R. Dupree, C. T. Forwood, and M. J. A. Smith, Phys. Status Solidi 24, 525 (1967).

[20] R. Monot, A. Chatelain, and J. P. Borel, Phys. Lett. 34A, 57 (1971).

[21] D. A. Gordon, R. F. Marzke, and W. S. Glausenger, J. Phys. (Paris) 38, C2-87 (1977).

[22] S. C. Jain and G. D. Sootha, Phys. Rev. 171, 1083 (1968).

[23] A. M. DeGraaf and A. W. Overhauser, Phys. Rev. 180, 701 (1969); A. W. Overhauser and A. M. DeGraaf, Phys. Rev. Lett. 22, 127 (1969).

[24] R. A. Moore, J. Phys. F 5, 459 (1975).

[25] M. Singh, J. Callaway, and C. S. Wang, Phys. Rev. B 14, 1214 (1976).

[26] F. Beuneu, J. Phys. F 10, 2875 (1980).

[27] F. Beuneu and P. Monod, Phys. Rev. B 18, 2422 (1978).

[28] R. A. Moore and C. F. Lui, Phys. Rev. B 8, 599 (1973).

[29] R. A. Moore, J. Phys. F 5, 2300 (1975).

[30] Y. Yafet, Solid State Phys. 14, 424 (1963).

[31] This assumption is not strictly valid for very small particles, but the variations of the lattice parameter are small and we do not expect them to affect our qualitative results. See, for example, J. L. Martins, R. Car, and J. Buttet, Surf. Sci. 106, 265 (1981).

[32] See, for example, Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1962).