Electron-Spin-Resonance Line Shape in Spherical Metal Particles*

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(Received 9 January 1967)

Dyson's theory of the electron-spin-resonance line shape for conduction electrons in metals has been extended for use with spherical particles in the region of normal skin effect. These more nearly correspond to typical samples, particularly so for naturally occurring metallic colloids. An explicit eigenfunction expansion is made for the fields and the magnetization, using eigenfunctions obtained from a Green's-function solution to the diffusion equation in this geometry. The line shapes vary roughly as in the one-dimensional case, and curves of this variation are shown to agree with experimental data for sodium.

I. INTRODUCTION

THE problem of the shape of electron-spin-resonance lines for conduction electrons in metals was investigated in 1955 by Dyson.[1] He treated the problem for plane samples of various skin depths, thicknesses, and relaxation times, and the measurements of Feher and Kip[2] confirmed his theory in reasonable detail. However, metallic ESR samples often consist of particles whose size is comparable to the skin depth in all dimensions. Examples of such samples are alkali metals dispersed in oil and naturally occurring colloids. This paper modifies Dyson's theory to treat spherical particles, supposed a fair approximation to actual samples. We assume normal skin effect.

The line shape is found in terms of the power absorbed at the surface of the particle:

$$P=(c/4\pi)\int \mathbf{E}\times\mathbf{H}^*\cdot d\mathbf{S}, \tag{1}$$

which may conveniently be converted to a surface impedance, $Z=P/4\pi a^2H_{10}^2$, where a is the particle radius and $\mathbf{H}_{10}$ the alternating field magnitude far from the particle. $\mathbf{H}_1$ near the particle consists of a term of order zero in the susceptibility, χ, plus linear and higher terms. We will derive the zeroth order $\mathbf{H}_1$ and $\mathbf{E}_1$ from a vector potential $\mathbf{A}_1$, and the linear terms from $\mathbf{A}_2$. Only terms linear in χ will be considered in P. Thus we neglect the nonresonant part of P, and contributions from terms quadratic and higher.

The calculation then proceeds in four stages: In Sec. II, we find $\mathbf{A}_1(\mathbf{r})$ from the boundary value problem with no magnetization. In Sec. III, we use Dyson's formulation to find $\mathbf{M}(\mathbf{r})$, the magnetization due to spins. This introduces the resonance, and requires a complete set of eigenfunctions, ψ_{lmn}, used to form a Green's function and to expand both $\mathbf{A}_1$ and $\mathbf{M}$. In Sec. IV: The first order Maxwell equations are inhomogeneous, since they include $\mathbf{M}$. A particular solution is found to the inhomogeneous equation, of the form $\mathbf{A}_2^p=\nabla\times\sum_{lmn}\psi_{lmn}(\mathbf{r})\,\mathbf{p}_{lmn}$. To this we add a solution of the homogeneous equation, $\mathbf{A}_2^h$. Outside the sphere we have merely Laplace's equation, with solution $\mathbf{A}_2^e$. We generate the coefficients of $\mathbf{A}_2^e$ by matching boundary conditions.

A word may be in order here on the use of $\mathbf{B}$ and $\mathbf{H}$: In free space (outside the sphere) these fields are identical. Inside, we decompose the vector potential according to powers of χ, so that $\nabla\times\mathbf{A}=\mathbf{B}$ yields

$$\nabla\times\mathbf{A}_1+\nabla\times\mathbf{A}_2+\cdots=\mathbf{H}_1+(\mathbf{M}+\mathbf{H}_2)+\cdots.$$

Thus we may say

$$\nabla\times\mathbf{A}_1=\mathbf{H}_1,\qquad \nabla\times\mathbf{A}_2=\mathbf{M}+\mathbf{H}_2,\quad \text{etc.}$$

Of course, outside the sphere $\mathbf{M}=0$, so our Poynting vector linear in χ may be evaluated just outside the surface, and is found in (V):

$$\mathbf{S}^{(1)}=\mathbf{A}_2^e\times(\nabla\times\mathbf{A}_1^*)+\mathbf{A}_1\times(\nabla\times\mathbf{A}_2^{e*}).$$

II. ZEROTH ORDER VECTOR POTENTIAL

Inside the particle, Maxwell's equations give

$$(\nabla^2+\beta^2)\mathbf{A}_1=0,\qquad r\le a, \tag{2}$$

where $\delta=(1+i)/\beta$ is the skin depth, and we have neglected the displacement current (the conductivity, $\sigma\gg\epsilon\omega$). Outside, $\sigma=0$, and

$$\nabla^2\mathbf{A}_1=0,\qquad r\ge a. \tag{3}$$

We assume for the internal vector potential

$$\mathbf{A}_1^i=\sum_{lm}\boldsymbol{\alpha}_{lm}\,j_l(\beta r)\,Y_l^m(\Omega) \tag{4}$$

and for the external one

$$\mathbf{A}_1^e=\sum_{lm}\{\boldsymbol{\beta}_{lm}r^e+\boldsymbol{\gamma}_{lm}r^{-l-1}\}Y_l^m(\Omega), \tag{5}$$

where $j_l(\beta r)$ are the spherical Bessel functions (of complex argument here) and Y_l^m are normalized spherical harmonics. (A factor of $e^{-i\omega t}$ is assumed for all fields). Since $\mathbf{M}=0$ in this order, both $\mathbf{A}_1$ and $\nabla\times\mathbf{A}_1$ are continuous at the boundary, and we take

$$\mathbf{A}_1^e(\infty)=-\tfrac{1}{2}H_{10}(\mathbf{r}\times\hat{\imath}) \tag{6}$$

* Supported in part by Research Corporation and National Science Foundation.

[1] F. J. Dyson, Phys. Rev. **98**, 349 (1955).
[2] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

as the imposed field ($\mathbf{H}_{10}$ is then in the x direction). Then

$$\mathbf{A}_1^i(\mathbf{r}) = -\frac{i(3\pi)^{1/2}H_{10}j_1(\beta r)}{\beta j_0(\beta a)} \times[\hat{\xi}_+ Y_1^0 - \hat{\xi}_0(Y_1^1+Y_1^{-1}) + \hat{\xi}_- Y_1^0], \quad (7)$$

where[3]

$$\hat{\xi}_\pm = \pm(\hat{\imath}\pm i\hat{\jmath})/\sqrt{2}, \qquad \hat{\xi}_0=\hat{k},$$
$$\hat{\xi}_\mu\cdot\hat{\xi}_{-\nu} = (-1)^\nu \hat{\xi}_\mu\cdot\hat{\xi}_\nu^* = (-1)^\nu\delta_{\mu\nu}. \quad (8)$$

We will need later

$$\nabla\times\mathbf{A}_1^i(\mathbf{r}) = \left(\frac{\pi}{10}\right)^{1/2} H_{10}\frac{j_2(\beta r)}{j_0(\beta a)}\{\hat{\xi}_+(Y_2^0-\sqrt{6}Y_2^{-2}) + \sqrt{3}\hat{\xi}_0(Y_2^{-1}-Y_2^1) - \hat{\xi}_-(Y_2^0-\sqrt{6}Y_2^2)\} + (\tfrac{2}{5}\pi)^{1/2}H_{10}(\hat{\xi}_- - \hat{\xi}_+)Y_0^0. \quad (9)$$

III. THE MAGNETIZATION

We wish to make expansions of the form

$$\mathbf{M}(\mathbf{r}) = \sum_{lmn}\mathbf{m}_{lmn}\psi_{lmn}(\mathbf{r})\,; \qquad \mathbf{m}_{lmn} = \int\psi_{lmn}^*\mathbf{M}d\tau, \quad (10)$$

where we choose the eigenfunctions ψ_{lmn} to satisfy the equation:

$$\nabla^2\psi_{lmn} = -(R_{lmn}/a)^2\psi_{lmn}, \quad (11)$$

with the boundary condition

$$\hat{n}\cdot\nabla\psi_{lmn}=0, \quad \text{at} \quad r=a. \quad (12)$$

The Green's function which is a solution to the diffusion equation for electrons of Fermi velocity v and mean free path Λ:

$$\tfrac{1}{3}(v\Lambda)\nabla^2G = \partial G/\partial t; \qquad \hat{n}\cdot\nabla G=0, \quad \text{at} \quad r=a, \quad (13)$$

can be written as

$$G(\mathbf{r},\mathbf{r}',t) = \sum_{lmn}\psi_{lmn}^*(\mathbf{r}')\psi_{lmn}(\mathbf{r})\exp[-\tfrac{1}{3}(v\Lambda)(R_{lmn}/a)^2t]. \quad (14)$$

We find

$$\psi_{lmn} = \left(\frac{2}{a^3}\frac{R_{lmn}^2}{R_{lmn}^2-l(l+1)}\right)^{1/2}\frac{j_l[R_{lmn}(r/a)]}{j_l(R_{lmn})}Y_l^m(\Omega), \qquad lmn\neq 0 \quad (15)$$

and

$$\psi_{000} = (3/a^3)^{1/2}Y_0^0, \quad (15a)$$

where

$$R_{lmn}j_{l-1}(R_{lmn}) = (l+1)j_l(R_{lmn}),$$
$$R_{lmn}j_{l+1}(R_{lmn}) = lj_l(R_{lmn}), \quad (16)$$

and

$$\int_{\text{Sphere}}\psi_{l'm'n'}^*\psi_{lmn}d\tau = \delta_{ll'}\delta_{mm'}\delta(R_{ln}-R_{ln'}), \quad (17)$$

as treated in detail in Appendix D. Only terms in $l=0$, and $l=2$ will be significant for our problem. For these values, Eq. (16) becomes

$$\tan R_{0n} = R_{0n},$$
$$\tan R_{2n} = R_{2n}(9-4R_{2n}^2)/(9-R_{2n}^2). \quad (18)$$

Dyson's formulation then results in a nonlocal equation which may be written:

$$\mathbf{m}_{lmn} = -i\omega_0\chi\{\eta_{lmn}^+(\hat{\xi}_-\cdot\mathbf{h}_{lmn})\hat{\xi}_+ - \eta_{lmn}^-(\hat{\xi}_+\cdot\mathbf{h}_{lmn})\hat{\xi}_-\}, \quad (19)$$

where

$$1/\eta_{lmn}^\pm = 1/T_1 + \tfrac{1}{3}(v\Lambda)(R_{lmn}^2/a^2) - i(\omega\mp\omega_0). \quad (20)$$

We will henceforth drop the η^- term, which represents the resonance from the counter-rotating circularly polarized component of our linear H_{10}. We may also ignore the subscript m in R_{lmn} and η_{lmn}, and we will write

$$1/\eta_{ln} = (R_{ln}^2 - w^2)/\tau, \quad (21)$$

$$w^2 = i(\omega-\omega_0)\tau - \tau/T_1, \qquad \tau = 2(a^2/\delta^2)T_D. \quad (22)$$

T_D, the time it takes a spin to diffuse across the skin depth, is

$$T_D = 3\delta^2/2v\Lambda. \quad (23)$$

[3] M. E. Rose, *Multipole Fields* (John Wiley & Sons, Inc., New York, 1955), p. 19.

Coefficients $\mathbf{h}_{lmn}$ are from

$$\nabla\times\mathbf{A}_1{}^i=\sum_{lmn}\mathbf{h}_{lmn}\psi_{lmn}, \tag{24}$$

that is

$$\mathbf{h}_{lmn}=\int_{\text{Sphere}}\psi_{lmn}{}^*(\nabla\times\mathbf{A}_1{}^i)\,d\tau. \tag{25}$$

In Appendix B it is shown that

$$\mathbf{m}_{00n}=-i\omega_0\chi\eta_{0n}(4\pi a^3)^{1/2}H_{10}F_0\hat{\xi}_+/(u^2-R_{0n}{}^2) \tag{26}$$

and

$$\mathbf{m}_{20n}=i\omega_0\chi\eta_{2n}(4\pi a^3)^{1/2}H_{10}F_2\hat{\xi}_+/(u^2-R_{2n}{}^2)(1-6/R_{2n}{}^2), \tag{27}$$

where $u=\beta a$, and

$$F_0=1-u\cot u, \tag{28}$$

$$F_2=(2/\sqrt{5})[3+F_0(1-9/u^2)]. \tag{29}$$

Also

$$\mathbf{m}_{2-2n}=-\sqrt{6}\mathbf{m}_{20n}. \tag{30}$$

All other $\mathbf{m}_{lmn}$'s vanish.

IV. FIRST-ORDER VECTOR POTENTIAL

At this point we have found $\mathbf{M}(\mathbf{r})$, but we must find the fields to which it gives rise in order to calculate the Poynting vector. The vector potential in this case satisfies

$$\nabla^2\mathbf{A}_2+\beta^2\mathbf{A}_2=-4\pi(\nabla\times\mathbf{M}),\qquad r\leq a, \tag{31}$$

and

$$\nabla^2\mathbf{A}_2=0,\qquad r\geq a. \tag{32}$$

As with $\mathbf{A}_1$, we choose the gauge

$$\nabla\cdot\mathbf{A}=0. \tag{33}$$

$$\mathbf{A}_2=\mathbf{A}_2{}^p+\mathbf{A}_2{}^h$$

inside, and $\mathbf{A}_2{}^e$ outside. We use

$$\mathbf{A}_2{}^p(\mathbf{r})=\nabla\times\sum_{lmn}\psi_{lmn}(\mathbf{r})\,\mathbf{p}_{lmn}, \tag{34}$$

$$\mathbf{A}_2{}^h(\mathbf{r})=\sum_{lm}\mathbf{a}_{lm}\,j_l(\beta r)\,Y_l{}^m, \tag{35}$$

$$\mathbf{A}_2{}^e(\mathbf{r})=\sum_{lm}\mathbf{c}_{lm}(a^{l+1}/r^{l+1})\,Y_l{}^m. \tag{36}$$

Now $\mathbf{A}_2{}^p(\mathbf{r})$ is a particular solution to Eq. (31), so

$$\mathbf{p}_{lmn}=-\frac{4\pi\mathbf{m}_{lmn}}{\beta^2-R_{ln}{}^2/a^2}. \tag{37}$$

The boundary conditions[4] for $\mathbf{A}_2$ and $\mathbf{H}_2$ are then used to find the coefficients $\mathbf{a}_{lm}$ and $\mathbf{c}_{lm}$:

$$\nabla\times[\mathbf{A}_2{}^p+\mathbf{A}_2{}^h-\mathbf{A}_2{}^e]=-4\pi\hat{r}\times[\hat{r}\times\mathbf{M}],\quad\text{at}\quad r=a, \tag{38}$$

$$\mathbf{A}_2{}^p+\mathbf{A}_2{}^h=\mathbf{A}_2{}^e,\quad\text{at}\quad r=a. \tag{39}$$

The gauge statement $\nabla\cdot\mathbf{A}=0$, for all $\mathbf{A}$, simplifies the problem also.

Further, it turns out that four of the coefficients $\mathbf{c}_{lm}$ are sufficient to express that part of the power (integral of the Poynting vector) with which we are concerned.

V. POWER

The first-order terms from (1) are

$$P^{(1)}=\frac{i\omega}{8\pi}\int[\mathbf{H}_2\cdot(\hat{r}\times\mathbf{A}_1{}^*)+(\nabla\times\mathbf{A}_1)\cdot(\hat{r}\times\mathbf{A}_2{}^*)]a^2d\Omega. \tag{40}$$

[4] J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., New York, 1962), pp. 9 and 154.

We evaluate the vector potentials and their curls at $r=a$, so we may conveniently use $\mathbf{A}_2^e(a)$ for $\mathbf{A}_2$ here, and therefore $\mathbf{H}_2=\nabla\times\mathbf{A}_2^e$. This results in

$$P^{(1)}=K[c^*+(3F_0/2u^2)c^*-(3F_0^*/2u^{2*})c], \tag{41}$$

where

$$K=\sqrt{2}\omega\omega_0\chi\tau H_{10}^2(\tfrac{4}{3}\pi a^3), \tag{42}$$

and

$$c=F_0^2G_0-(\tfrac{7}{4})F_2^2G_2. \tag{43}$$

Here

$$G_0=\sum_n[(u^2-R_{0n}^2)^2(R_{0n}^2-w^2)]^{-1}, \tag{44}$$

and

$$G_2=\sum_n[(u^2-R_{2n}^2)^2(R_{2n}^2-w^2)(1-6/R_{2n}^2)]^{-1}. \tag{45}$$

VI. COMPARISON TO DYSON'S RESULT

Dyson's general result [his Eqs. (71)-(73)] is, in similar notation,

$$P^{(1)}=\tfrac{1}{4}\omega\omega_0\chi H_{10}^2\tau F_D^2G_D\cdot(\text{Volume}), \tag{46}$$

where $F_D=-u\tan u$. These all have the same behavior in the limits of small and large u:

Large u: $F_0\simeq F_2\simeq F_D\simeq iu$

Small u: $F_0\simeq\tfrac{1}{3}u^2$, $F_2\simeq(16/15\sqrt{5})u^2$, $F_D\simeq -u^2$.

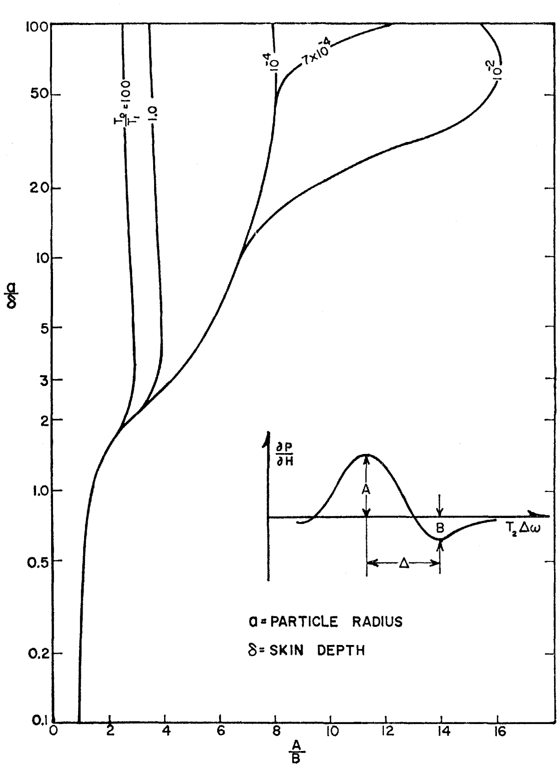

FIG. 1. A/B versus a/δ for the derivative of the absorption signal, for a sequence of values of T_D/T_1.

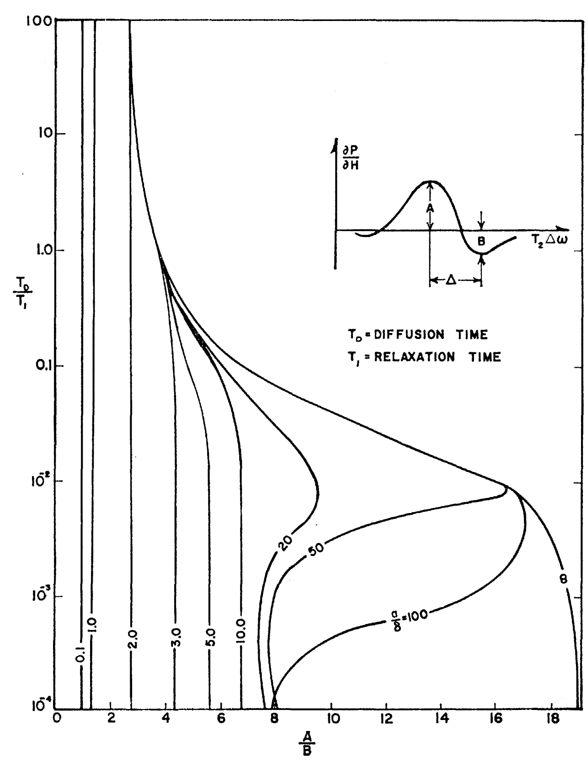

FIG. 2. A/B versus T_D/T_1 for the derivative of the absorption signal, for various values of a/δ. The curve for $a/\delta=\infty$ corresponds to that obtained by Feher and Kip using Dyson's theory

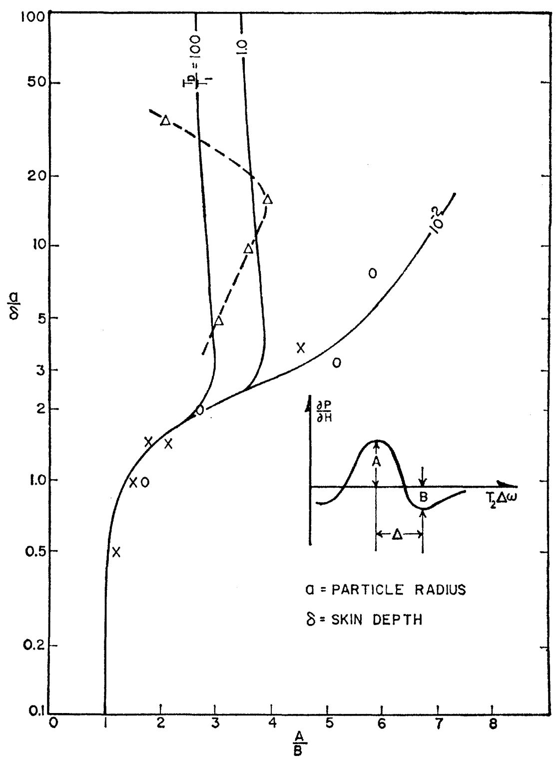

FIG. 3. Some experimental data compared to one of the curves of Fig. 1. Crosses-300°K, circles-77°K, triangles-4.2°K. δ is not reliable at 4.2°K.

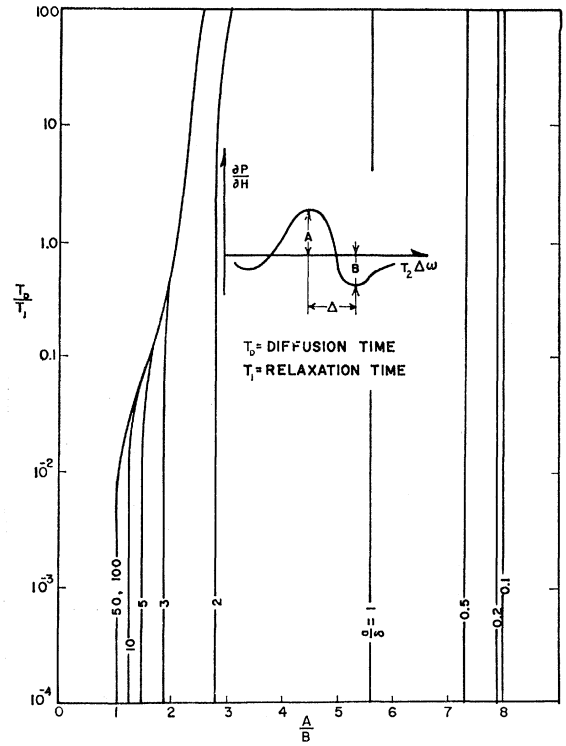

FIG. 5. A/B versus T_D/T_1 for the derivative of the dispersion signal, for various values of a/δ.

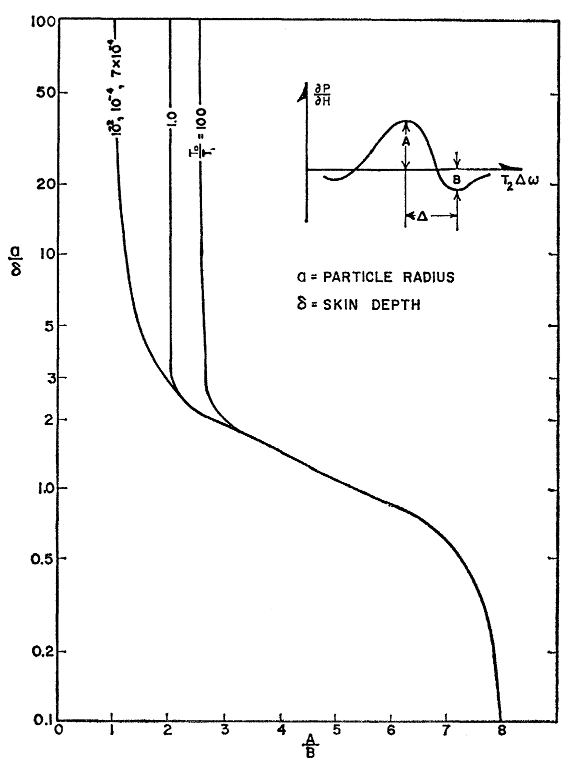

FIG. 4. A/B versus a/δ for the derivative of the dispersion signal, for a sequence of values of T_D/T_1.

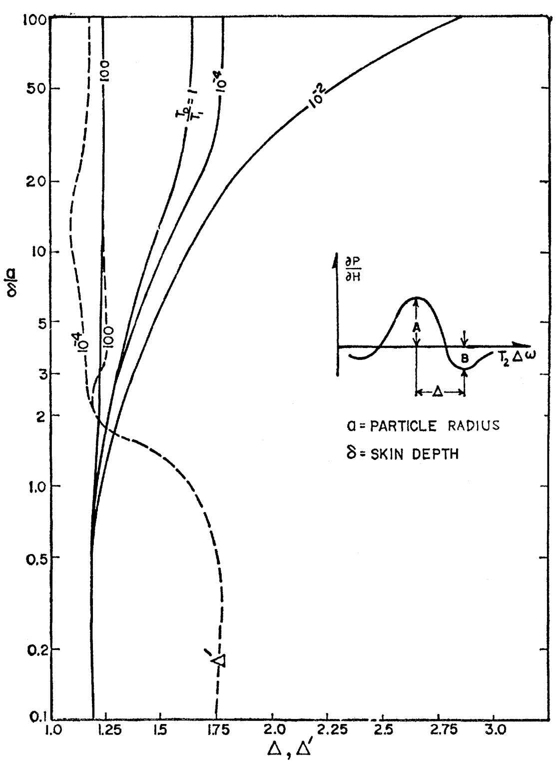

FIG. 6. Linewidths versus a/δ. Δ refers to absorption, Δ' to dispersion.

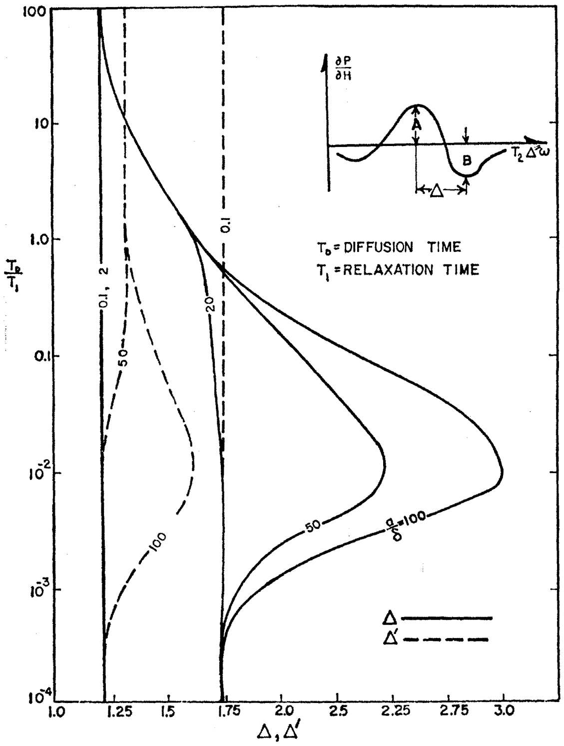

FIG. 7. Linewidths versus T_D/T_1. Here Δ refers to absorption, Δ' to dispersion.

Dyson's G_D is the same as our G_0, except that R_{0n} is replaced by $n\pi$ (which is the limiting value of R_{ln} for large n).

Thus the general form of the result is the same, as expected. This is confirmed by the results shown in the next section.

VII. LINE SHAPE

The line shape given by Eq. (41) is very similar to that found by Dyson. In the limits of large and small u, the two calculations give identical results. The behavior of the line shape as a function of a/δ and of T_D/T_1 is given in Figs. 1 and 2. Figure 2 should be compared to Fig. 7 in the paper of Feher and Kip. The parameter A/B is a particularly useful one for comparison with experimental results. The curve in Fig. 2 labeled ∞ is the one pertinent to Dyson's theory.

One is struck by the behavior of the curves for large a/δ in the region of small T_D/T_1. This return toward symmetry is a consequence of the fact that, although the skin layer is a small fraction of the particle volume the spin crosses the particle in a time short compared to T_1 and therefore spends more time in the skin layer than in the case of the semi-infinite metal. This situation is not considered by Feher and Kip. Dyson also excludes it, since he assumes T_D/T_1 is never smaller than 10^{-2}. The samples used in selective transmission experiments[5,6] are of this size, although in that technique the transmission line shape is not handled by this theory or that of Dyson.

Figure 3 is similar to Fig. 1, with experimental data from a graded sequence of sodium particles. These are known to have been nearly spherical, but their surface is neither very smooth (cf. Feher and Kip[2]) nor, perhaps, is it unaffected by the soaplike molecules which are attached to it in the oil. The fit here is in accord with Dyson's conclusions that surface relaxation should play a minimal role in the line shape for the alkalis. If this is not true at low temperatures, as suggested by Schultz and Latham,[5] then fits like that of Fig. 3 can give the required information regarding the relaxation. The data at 4.2 deg should be regarded as preliminary, and their interpretation awaits a careful inclusion of the effects of the anomalous skin effects on this theory. A further complication at these temperatures is that the mean-free path is comparable to the particle size. It is probably this which is responsible for the anomaly in the helium temperature data, although the curves for large a/δ and very small T_D/T_1 are suggestive, since $T_D/T_1 \propto (\mathrm{Temp})^3$.

It should be emphasized that the data presented here are intended to show that the behavior of the line shape as a function of size is accounted for by the present calculation. The study of T_D and T_1 in these particles, which motivates this calculation, is left for a later article. At present, we find Fig. 1 most useful in estimating particle sizes, a tedious job when done with a microscope. Figures 4, 5, 6, and 7 may prove useful to workers in this field.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor A. E. Everett and Professor L. M. Roth for their continued interest and invaluable help with various aspects of this problem. Thanks are also due the Tufts Computation Center, which provided computer time.

APPENDIX A: THE EIGENFUNCTIONS

The Green's function satisfies

$$\tfrac{1}{3}(v\Lambda)\nabla^2 G(\mathbf{r},\mathbf{r}',t) = (\partial/\partial t)G(\mathbf{r},\mathbf{r}',t), \qquad \text{(A1)}$$

when subject to the boundary condition

$$\hat{r}\cdot G(\mathbf{r},\mathbf{r}',t) = 0, \quad \text{at} \quad r=a. \qquad \text{(A2)}$$

Further, we expect it to have the form[7]

$$G(\mathbf{r},\mathbf{r}',t) = \sum_{lmn} e^{-\lambda t}\psi_{lmn}(\mathbf{r})\psi_{lmn}^*(\mathbf{r}'). \qquad \text{(A3)}$$

We will write

$$\psi_{lmn}(\mathbf{r}) = b_{lmn} j_l[R_{ln}(r/a)]Y_l^m(\vartheta,\varphi), \qquad \text{(A4)}$$

[5] S. Schultz and C. Latham, Phys. Rev. Letters **15**, 148 (1965).

[6] R. B. Lewis and T. R. Carver, Phys. Rev. Letters **12**, 693 (1964). N. S. Vander Ven and R. T. Schumacher, *ibid.* **12**, 695 (1964).

[7] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1950), p. 314.

using the analogy of a general expansion for $G(\mathbf{r})$, with the term in h_l suppressed, since it is not finite at $r=0$. The j_l are spherical Bessel functions and the Y_l^m are normalized spherical harmonics.

Clearly,

$$\nabla^2\psi_{lmn}(\mathbf{r}) = -(R_{nl}/a)^2\psi_{lmn}(\mathbf{r}), \tag{A5}$$

so this $G(\mathbf{r}, \mathbf{r}', t)$ does indeed satisfy (A1), and in (A3)

$$\lambda = \tfrac{1}{3}(v\Lambda)(R_{nl}^2/a^2). \tag{A6}$$

We now apply (A2)

$$\hat{r}\cdot\nabla G = \sum_{lmn} e^{-\lambda t}\psi_{lmn}^*(\mathbf{r}')b_{lmn}Y_l^m(\vartheta,\varphi)(\partial/\partial r)j_l(R_{ln}/ar)\big]_{r=a} = 0.$$

Therefore

$$(\partial/\partial r)j_l(R_{ln}/ar)\big]_{r=a} = 0, \tag{A7}$$

which is the defining equation for R_{ln}. We now require that our eigenfunctions be orthonormal

$$\int_{\text{Sphere}} \psi_{l'm'n'}^*(\mathbf{r})\psi_{lmn}(\mathbf{r})r^2dr\,d\Omega = \delta_{ll'}\delta_{mm'}\delta(R_{ln}-R_{ln'}). \tag{A8}$$

The spherical harmonics assure us of orthogonality as regards l, l' and m, m'. Therefore

$$\int_0^a b_{lmn}b_{lmn'}^*j_l\left(\frac{R_{ln}}{a}r\right)j_l\left(\frac{R_{ln}'}{a}r\right)r^2dr = \delta(R_{ln}-R_{ln'}). \tag{A9}$$

For $n\neq n'$, using the Lommel integral and Eq. (A7), we verify that

$$\int_0^a j_l(\alpha r)j_l(\beta r)r^2dr = 0.$$

The more useful case is $n=n'$:

$$|b_{lmn}|^2\int_0^a j_l^2\left(\frac{R_{ln}}{a}r\right)r^2dr = |b_{lmn}|^2 j_l^2(R_{ln})\left[1-\frac{l(l+1)}{R_{ln}^2}\right]\tfrac{1}{2}a^2,$$

hence

$$\psi_{lmn}(\mathbf{r}) = \left(\frac{2/a^3}{1-l(l+1)/R_{ln}^2}\right)^{1/2}\frac{j_l[R_{ln}(r/a)]}{j_l(R_{ln})}Y_l^m(\vartheta,\varphi), \tag{A10}$$

where we have set an arbitrary phase factor equal to unity.

We find ψ_{000}, from (A8), to be $1/(\text{Volume})^{1/2} = (3/a^3)^{1/2}Y_0^0$. This contributes a constant term to G and may be thought of as the term in the probability distribution corresponding to nondiffusing spins.

These eigenfunctions may also be obtained by the method of Laplace transforms, and were so found originally.

APPENDIX B: THE MAGNETIZATION

The magnetization is found by a straightforward application of the method suggested by Dyson: The expansion coefficients of the magnetic field $\mathbf{H}_1$ are

$$\mathbf{h}_{lmn} = \int\psi_{lmn}^*(\nabla\times\mathbf{A}_1^i)d\tau, \tag{B1}$$

where we use

$$\nabla\times\mathbf{A}_1^i = (2\pi/5)^{1/2}H_{10}(\hat{\xi}_- - \hat{\xi}_+)Y_0^0 + (\pi/10)^{1/2}H_{10}j_2(\beta r)/j_0(\beta a)\{\hat{\xi}_+(Y_2^0-\sqrt{6}Y_2^{-2})+\sqrt{3}\hat{\xi}_0(Y_2^{-1}-Y_2^1)-\hat{\xi}_-(Y_2^0-\sqrt{6}Y_2^2)\}. \tag{B2}$$

Therefore

$$\mathbf{h}_{00n} = \left(\frac{2\pi}{5}\right)^{1/2}H_{10}\left(\frac{2}{a^3}\right)^{1/2}(\hat{\xi}_- - \hat{\xi}_+)\int_0^a j_0(\beta r)j_0(R_{0n}r/a)r^2dr/j_0(R_{0n})$$
$$= (4\pi a^3)^{1/2}H_{10}(\hat{\xi}_- - \hat{\xi}_+)(1-u\cot u)/(u^2-R_{0n}^2), \tag{B3}$$

$$\mathbf{h}_{00n} \equiv h_{00n}(\hat{\xi}_- - \hat{\xi}_+). \tag{B4}$$

Similarly,

$$\mathbf{h}_{20n} = \left(\frac{\pi}{5a^3}\frac{R_{2n}^2}{R_{2n}^2-6}\right)^{1/2}\frac{H_{10}(\hat{\xi}_+ - \hat{\xi}_-)}{j_0(u)j_2(R_{2n})}\int_0^a j_2(\beta r)j_2[R_{2n}(r/a)]r^2dr$$
$$= \left(\frac{4\pi a^3R_{2n}^2}{R_{2n}^2-6}\right)^{1/2}\frac{H_{10}(\hat{\xi}_+ - \hat{\xi}_-)F_2}{u^2-R_{2n}^2}, \tag{B5}$$

where

$$F_2=2[3+F_0(1-9/u^2)]/\sqrt{5}, \qquad F_0=1-u\cot u. \tag{B6}$$

Again,

$$\mathbf{h}_{20n}\equiv h_{20n}(\hat{\xi}_- - \hat{\xi}_+). \tag{B7}$$

Then

$$\mathbf{h}_{22n}=-\sqrt{6}h_{20n}\hat{\xi}_-, \tag{B8}$$

and

$$\mathbf{h}_{2-2n}=-\sqrt{6}h_{20n}\hat{\xi}_+. \tag{B9}$$

We may then find the expansion coefficients, using Eq. (19)

$$\begin{aligned}\mathbf{m}_{lmn}\cdot\hat{\xi}_- &= i\omega_0\chi\eta_{lmn}{}^+(\hat{\xi}_-\cdot\mathbf{h}_{lmn})\\ &= i\omega_0\chi\{\eta_{0n}{}^+h_{00n}+(1-\sqrt{6})\eta_{2n}{}^+h_{20n}\}.\end{aligned} \tag{B10}$$

Now here we shall explicitly assume that the resonance is narrow enough so that when η^+ is large, the term in η^- is negligible. Thus

$$\mathbf{m}_{lmn}=m_{lmn}\hat{\xi}_+=-(\mathbf{m}_{lmn}\cdot\hat{\xi}_-)\hat{\xi}_+. \tag{B11}$$

Then the only nonvanishing m_{lmn} are

$$m_{00n}=-i\omega_0\chi\eta_{0n}h_{00n}=-\frac{i\omega_0\chi(4\pi a^3)^{1/2}H_{10}\tau F_0}{(u^2-R_{0n}{}^2)(R_{0n}{}^2-w^2)}, \tag{B12}$$

$$m_{20n}=-i\omega_0\chi\eta_{2n}h_{20n}=+\frac{i\omega_0\chi(4\pi a^3)^{1/2}H_{10}\tau F_2}{(1-6/R_{2n}{}^2)^{1/2}(u^2-R_{2n}{}^2)(R_{2n}{}^2-w^2)}, \tag{B13}$$

and

$$m_{2-2n}=-\sqrt{6}m_{20n}. \tag{B14}$$

APPENDIX C: THE COEFFICIENTS OF $\mathbf{A}_2{}^e$

Section IV gives the boundary conditions on $\mathbf{A}_2$

$$\nabla\times[\mathbf{A}_2{}^p+\mathbf{A}_2{}^h-\mathbf{A}_2{}^e]=-4\pi\hat{r}\times[\hat{r}\times\mathbf{M}], \qquad r=a \tag{C1}$$

$$\mathbf{A}_2{}^p+\mathbf{A}_2{}^h-\mathbf{A}_2{}^e=0, \qquad r=a, \tag{C2}$$

$$\nabla\cdot\mathbf{A}_2=0. \tag{C3}$$

And we will use:

$$\mathbf{A}_2{}^p(\mathbf{r})=-\nabla\times\sum_{lmn}\frac{4\pi a^2\mathbf{m}_{lmn}}{u^2-R_{2n}{}^2}\psi_{lmn}(\mathbf{r}), \tag{C4}$$

$$\mathbf{A}_2{}^h(\mathbf{r})=\sum_{lm}\mathbf{a}_{lm}j_l(\beta r)Y_l{}^m, \tag{C5}$$

$$\mathbf{A}_2{}^e(\mathbf{r})=\sum_{lm}\mathbf{c}_{lm}(a/r)^{l+1}Y_l{}^m. \tag{C6}$$

Since the solutions are for $r=a$, we need only multiply by $Y_L{}^{M*}$ and integrate over the surface of the sphere to find relations among the coefficients. Further, Appendix D will show that only $c_{10}{}^+$, $c_{10}{}^-$, $c_{11}{}^0$, and $c_{1-1}{}^0$ will be needed. $c_{lm}{}^+\equiv\hat{\xi}_+\cdot\mathbf{c}_{lm}$.

We will need expressions for the divergence and curl of our vector potentials. They follow the general form:

$$\nabla j_l(qr)Y_l{}^m=\left(\frac{l+1}{2l+1}\right)^{1/2}qj_{l+1}(qr)\mathbf{T}_{l,l+1}{}^m+\left(\frac{l}{2l+1}\right)^{1/2}qj_{l-1}(qr)\mathbf{T}_{l,l-1}{}^m, \tag{C7}$$

where the vector spherical harmonics[8] may be written as

$$\mathbf{T}_{l,l\pm1}{}^m=\sum_\mu c(l\pm1,1,l;m+\mu,-\mu)Y_{l\pm1}{}^{m+\mu}\hat{\xi}_{-\mu},$$

in terms of the Clebsch-Gordon coefficients.

Applying Eq. (C2) we find:

$$a_{10}{}^+j_1(u)=c_{10}{}^+, \tag{C8}$$

$$a_{10}{}^-j_1(u)=c_{10}{}^-+2(\tfrac{3}{5})^{1/2}Q, \tag{C9}$$

$$a_{11}{}^0j_1(u)=c_{11}{}^0-(\tfrac{3}{5})^{1/2}Q, \tag{C10}$$

$$a_{1-1}{}^0j_1(u)=c_{1-1}{}^0+6(\tfrac{3}{5})^{1/2}Q, \tag{C11}$$

[8] M. E. Rose, *Multipole Fields* (John Wiley & Sons, Inc., New York, 1955) p. 22.

where

$$Q=4\pi i(2/a)^{1/2}\sum_n m_{20n}[(1-6/R_{2n}^2)^{1/2}(u^2-R_{2n}^2)]^{-1}. \quad \text{(C12)}$$

We next use the gauge condition to show that

$$c_{10}^{+}=c_{11}^{0}, \qquad c_{10}^{-}=c_{1-1}^{0}. \quad \text{(C13)}$$

Finally, our last two equations come from the $\hat{\xi}_+$ and $\hat{\xi}_-$ components of Eq. (C1), with $L=M=0$:

$$i(1/\sqrt{3})uj_0(u)[a_{10}^{+}+a_{1-1}^{0}]-(\tfrac{2}{15})^{1/2}\sum_n \frac{4\pi(2/a^3)^{1/2}(9-R_{2n}^2)m_{2-2n}}{(u^2-R_{2n}^2)(1-6/R_{2n}^2)^{1/2}}=-4\pi(\tfrac{2}{15})^{1/2}\sum_n\left(\frac{2/a^3}{1-6/R_{2n}^2}\right)^{1/2} m_{2-2n}, \quad \text{(C14)}$$

$$-i(1/\sqrt{3})uj_0(u)[a_{11}^{0}+a_{10}^{-}]-\tfrac{4}{3}\pi\left(\frac{2}{5a^3}\right)^{1/2}\sum_n\frac{(9-R_{2n}^2)m_{20n}}{(u^2-R_{2n}^2)(1-6/R_{2n}^2)^{1/2}}$$

$$+\tfrac{2}{3}4\pi\left(\frac{2}{a^3}\right)^{1/2}\sum_n\frac{m_{00n}R_{0n}^2\epsilon_n}{u^2-R_{0n}^2}=-\tfrac{4}{3}\pi\left(\frac{2}{5a^3}\right)^{1/2}\sum_n\frac{m_{20n}}{(1-6/R_{2n}^2)^{1/2}}-\tfrac{2}{3}4\pi\left(\frac{2}{a^3}\right)^{1/2}\sum_n m_{00n}\epsilon_n, \quad \text{(C15)}$$

$$\epsilon_n=(\sqrt{3}/\sqrt{2}) \quad \text{if} \quad n=0,$$

$$\epsilon_n=1 \qquad \text{otherwise.}$$

These eight equations then yield

$$c_{10}^{+}+c_{10}^{-}=4\pi a\omega_0\chi H_{10}\tau(\tfrac{8}{3}\pi)^{1/2}(F_0^2G_0-\tfrac{7}{4}F_2^2G_2). \quad \text{(C16)}$$

The factor in parentheses is then the c of Eq. (41), and the rest is included in K.

APPENDIX D: POWER

The power absorbed by the resonance is calculated by an integration of the terms in the Poynting vector which are linear in χ:

$$P^{(1)}=\frac{i\omega}{8\pi}\int[(\nabla\times\mathbf{A}_2)\cdot(\hat{r}\times\mathbf{A}_1^*)+(\nabla\times\mathbf{A}_1)\cdot(\hat{r}\times\mathbf{A}_2^*)]a^2d\Omega. \quad \text{(D1)}$$

We already know $\mathbf{A}_1$ and $\nabla\times\mathbf{A}_1$, which give, at $r=a$:

$$\hat{r}\times\mathbf{A}_1=-(\tfrac{1}{5}\pi)^{1/2}(H_{10}aF_0/u^2)[\hat{\xi}_+(\sqrt{6}Y_2^{-2}-Y_2^0-2\sqrt{5}Y_0^0)-\hat{\xi}_-(\sqrt{6}Y_2^2-Y_2^0-2\sqrt{5}Y_0^0)+\sqrt{3}\hat{\xi}_0(Y_2^1-Y_2^{-1})] \quad \text{(D2)}$$

and

$$\nabla\times\mathbf{A}_1=(\tfrac{2}{3}\pi)^{1/2}H_{10}(\hat{\xi}_--\hat{\xi}_+)Y_0^0$$

$$+(\tfrac{1}{10}\pi)^{1/2}H_{10}[(3F_0-u^2)/u^2][\hat{\xi}_+(Y_2^0-\sqrt{6}Y_2^{-2})+\sqrt{3}\hat{\xi}_0(Y_2^{-1}-Y_2^1)-\hat{\xi}_-(Y_2^0-\sqrt{6}Y_2^2)]. \quad \text{(D3)}$$

For $\mathbf{A}_2$ we will use $\mathbf{A}_2^e$:

$$\hat{r}\times\mathbf{A}_2^e=-\sum_{lm}\mathbf{c}_{lm}\times\left[\left(\frac{l+1}{2l+1}\right)^{1/2}\mathbf{T}_{l,l+1}^{m}-\left(\frac{l}{2l+1}\right)^{1/2}\mathbf{T}_{l,l-1}^{m}\right], \quad \text{(D4)}$$

and

$$\nabla\times\mathbf{A}_2^e=-a^{-1}\sum_{lm}[(l+1)(2l+1)]^{1/2}\mathbf{c}_{lm}\times\mathbf{T}_{l,l+1}^{m}. \quad \text{(D5)}$$

In the first term of (D1) we have integrals of Y_{l+1} times Y_2^* or Y_0^*, so only the coefficients found in Appendix C will occur. This term then simplifies to

$$P^{(1)}(\text{1st term})=-\frac{(3\pi)^{1/2}\omega a^2H_{10}}{4\pi}\frac{F_0^*}{u^{2*}}(c_{10}^{+}+c_{10}^{-}). \quad \text{(D6)}$$

The second term is more tedious, since it contains a variety of c_{3m}^{μ}'s. However, these terms all neatly cancel, as is shown most easily by grouping terms in the calculation. The rest of the expression behaves like the first term, and we find

$$P^{(1)}(\text{2nd term})=[(3\pi)^{1/2}\omega a^2H_{10}/4\pi][(F_0/u^2)+\tfrac{2}{3}](c_{10}^{+}+c_{10}^{-})^*. \quad \text{(D7)}$$

Thus,

$$P^{(1)}=K\{c^*+\tfrac{3}{2}(F_0/u^2)c^*-\tfrac{3}{2}(F_0^*/u^{2*})c\}, \quad \text{(D8)}$$

where

$$K=\sqrt{2}\omega\omega_0\chi\tau H_{10}^2(\tfrac{4}{3}\pi a^3). \quad \text{(D9)}$$