FIG. 3. The functions $F(S, v^*)$ and $\xi(S, v^*)$ for spherical symmetry.

ples for a range of S values are plotted in Figs. 1-3.

For many purposes, it is desirable and sufficient to use analytical approximations for these functions.

The interpolation formulas

$$F(S, v^*) = (2/\pi)^2 \left\{ [1 + (v^{*1/\mu} - 1) \sqrt{S}]^3 - 1 \right\} \qquad (5)$$

and

$$\xi^2(S, v^*) = S[1 - (1 + F)^{-2/3}] \qquad (6)$$

connect the asymptotic behavior at $v^{*1/\mu}\sqrt{S} \gg 1$ with the proper limit at $v^* = 1$.[5] When inserted in Eq. (1), they approximate the exact Γ_p to $\lesssim 20\%$ over parameter ranges of interest.

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Knight Shift in Small Particles at Low Temperatures*

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It is shown that the magnetic moments of the O_2 molecules in a surface layer of air adsorbed to small particles will create a static magnetic field at low temperatures that is large enough to affect the measured Knight shifts and linewidths.

It is the purpose of this note to point out that if a layer of air is adsorbed to the surfaces of small particles (dimensions on the order of hundreds of Angstroms or less) it will affect the measured Knight shifts and linewidths at low temperatures. This happens because the magnetic dipole moments of the O_2 molecules in the layer of air are sufficiently polarized at low temperatures that they create a magnetic field inside the particle that is in many cases on the order of the inherent Knight shift.

The static magnetic field $H(O_2)$ created inside a small particle by the O_2 molecules adsorbed on its surface will now be calculated. A typical particle is in the form of a cylindrical platelet. For the purpose of calculation the external field H_0 is in the x direction. The axis of the cylinder is along the x axis and the cylinder has a length l. The two circular disc ends of the cylinder are located at $x = 0$ and $x = l$ and have a diameter d. It is obvious that only the component of $H(O_2)$ in the x direction, $H_x(O_2)$, will contribute to an observed shift. It is further assumed that $H_x(O_2)$ does not vary in the plane perpendicular to the x axis. This is a reasonable assumption for the order-of-magnitude calculation that is being made. (For example, the field from the O_2 dipoles on the flat end

surfaces has a minimum value at $y = \frac{1}{2}d$ which is about 50% of its maximum value which is at $y = 0$.) Under these assumptions it is only necessary to calculate $H_x(O_2)$ along the x axis.

The calculation is in two parts. First, the contribution to $H_x(O_2)$ by the O_2 dipoles on the two flat circular plates of diameter d at $x = 0$ and $x = l$ is calculated. An annular ring of radius y and width dy on the flat surface at $x = 0$ creates a field

$dH_x(O_2$ on annular ring)

$$= [2\pi yN\langle\mu_{O_2}\rangle (3\cos^2\theta - 1)dy]/(x^2 + y^2)^{3/2}, \quad (1)$$

where N is the number of O_2 magnetic dipoles per cm^2, $\langle\mu_{O_2}\rangle$ is the statistical-mechanical expectation value of the magnetic moment of an O_2 molecule, and θ is the angle between the x axis and the annular ring. Equation (1), integrated over the two surfaces at $x = 0$ and $x = l$, gives

$H_x(O_2$ on surfaces at $x = 0$ and $x = l)$

$$= \frac{\pi Nd^2\langle\mu_{O_2}\rangle}{2(x^2 + \frac{1}{4}d^2)^{3/2}} + \frac{\pi Nd^2\langle\mu_{O_2}\rangle}{2[(l - x)^2 + \frac{1}{4}d^2]^{3/2}}. \quad (2)$$

The second part of the calculation is to find the field along the x axis from the layer of dipoles on the cylindrical surface. This is easiest to do if the dipole layer is replaced by two sheets of current circulating in opposite directions and separated by the diameter of an O_2 molecule. The contribution to $H_x(O_2)$ from the dipoles on the cylindrical surface is found by subtracting the field created by the current sheet with a radius $\frac{1}{2}d$ from the field of a cylindrical current sheet with a radius $\frac{1}{2}d$ minus the diameter of an O_2 molecule. Thus,

$H_x(O_2$ on cylindrical surface$) = -2\pi dN\langle\mu_{O_2}\rangle$

$$\times \{x/(x^2 + \frac{1}{4}d^2)^{3/2} + (l - x)/[(l - x)^2 + \frac{1}{4}d^2]^{3/2}\}. \quad (3)$$

Adding Eqs. (2) and (3) gives for the total field produced by all the O_2 dipole moments H_x (all O_2),

$H_x(\text{all } O_2) = \pi Nd\langle\mu_{O_2}\rangle$

$$\times \left(\frac{\frac{1}{2}d - x}{(x^2 + \frac{1}{4}d^2)^{3/2}} + \frac{(\frac{1}{2}d - l + x)}{[(l - x)^2 + \frac{1}{4}d^2]^{3/2}}\right). \quad (4)$$

This internal static field will give rise to a shift $\langle H_x(O_2)\rangle_{av}/H_0$, which is the average field inside the platelet divided by the external field. Equation (4), averaged over the x axis, yields a shift

shift $= \langle H_x(O_2)\rangle_{av}/H_0 = \pi N\langle\mu_{O_2}\rangle/lH_0$

$$\times [4l + 2d - 4(l^2 + \frac{1}{4}d^2)^{1/2}]/(l^2 + \frac{1}{4}d^2)^{1/2}. \quad (5)$$

Consider the case where there are a large number of platelets spread over a range of diameters. This means that the correct shift is obtained by averaging over d in Eq. (5). If, for example, there are platelets varying in diameter from $d = \frac{5}{2}l$ to $d = 5l$, Eq. (5) gives a shift that varies from $4.2\pi N\langle\mu_{O_2}\rangle/d_{\min}$ for the minimum-diameter particle to $6\pi N\langle\mu_{O_2}\rangle/d_{\max}$ for the maximum-diameter particle. Since the average shift lies between these two values,

$$\text{shift} = \frac{1}{2}\pi N\mu_{O_2}^2/kT (4.2/d_{\min} + 6/d_{\max}). \quad (6)$$

The relationship $\langle\mu_{O_2}\rangle \approx \mu_{O_2}^2 H_0/kT$ was used in arriving at Eq. (6) since usually $\mu_{O_2}H_0/kT < 1$.

The predicted shift (6) is inversely proportional to the size of the particle and is independent of the external magnetic field.

An examination of Eq. (4) will show that $H_x(O_2)$ does not vary much inside the particle (less than 10% for particle configurations considered here). On the other hand, there is a large variation (about 50%) of $\langle H_x(O_2)\rangle_{av}$ between the largest- and smallest-diameter particle. Thus, the linewidth is the difference between $\langle H_x(O_2)\rangle_{av}$ in the smallest-diameter particle and $\langle H_x(O_2)\rangle_{av}$ in the largest-diameter particle. Consequently, Eq. (5) gives a linewidth,

$$\text{linewidth} = \pi N\mu_{O_2}^2 H_0/kT (4.2/d_{\min} - 6/d_{\max}). \quad (7)$$

The predicted linewidth, Eq. (7), is proportional to the magnetic field, inversely proportional to the particle size, and inversely proportional to the temperature.

It is possible that not every particle will have its axis parallel to the external field. For particles with axes at a nonzero angle with respect to the field there will still be a shift. The calculation is more complicated but is not necessary since qualitatively it appears that the shift does not vary much with angle as can be seen by replacing the curved surfaces by flat surfaces and estimating the fields produced.

It is of interest to see what magnitudes Eqs. (6) and (7) predict for the line shift and linewidth. Let us assume that the external field varies from 1200 to 8800 G, the particles have diameters ranging from $d_{\min} = 100$ Å to $d_{\max} = 200$ Å, and a length of 40 Å; the minimum temperature is $T_{\min} = 1.5$°K, and $\mu_{O_2} = 2\times10^{-20}$ erg/G. Assuming that $\frac{1}{5}$ of the layer of air is O_2 and that the diameter of an O_2 molecule is 4 Å, N is found to be $5\times10^{14}/\pi$ O_2 molecules/cm^2. With these values Eqs. (6) and (7) give a

predicted shift = 0.33%,
predicted linewidth = 0.10% H_0. $\quad (8)$

The results, Eqs. (8), are on the order of the values of the Knight shifts and linewidths measured for small superconducting particles.[1] For $T \ll T_c$ the superconducting transition temperature, the

Knight shift is expected to vanish, yet most experiments at these low temperatures have found an anomalous "shift" that is about $\frac{2}{3}$ of its value in the normal state. For example, Androes and Knight[1] found at $T \ll T_c$ a shift = 0. 55% and a linewidth = 0. 34% H_0. Equations (8), which were derived by using the numerical quantities that correspond to the experiments of Androes and Knight, agree favorably with their results. This means that in order to measure the true Knight shift for small particles at low temperatures steps must be taken to keep a layer of air (or layer of any paramagnetic molecules) from adsorbing to the particle's surfaces.

The spin-lattice relaxation time also has often shown anomalous behavior below T_c for superconducting particles less than 1μ in size.[2] If there is a layer of air on the surfaces of the small particles, most of the superconducting nuclei will be within several hundred Å of an O_2 molecule on the surface. This suggests that the anomalous relaxation that has been observed for the superconducting nuclei is due to the combination of direct relaxation of the nuclei by the surface O_2 and nuclear spin diffusion. Evidence that this effect might be present is the experimental work on nonconducting solids where nuclei are relaxed by paramagnetic impurities several hundred Å away, and the nuclear relaxation times measured are often on the order of those observed in small superconducting particles.[3] Thus, in order to eliminate this source of anomalous relaxation in small superconducting particles all O_2 (or other paramagnetic impurities) must be removed from the particle's surfaces.

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Paramagnetic Curie Temperatures of the Rare-Earth Monophosphides†

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We show how it is possible to understand the sign change of the paramagnetic Curie temperatures in going from the light to heavy rare-earth monophosphides.

The paramagnetic Curie temperatures Θ_p of the rare-earth monophosphides REP have recently been determined by Jones.[1] The striking feature of his results is the change in sign of the temperatures Θ_p in going from the light to heavy rare earths. The paramagnetic Curie temperature derived from the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction together with the spherical band approximation is proportional to[2]

$$k\Theta_p \propto Z^2 (g_J - 1)^2 J(J+1) \, \Gamma^2 E_F^{-1} \sum_m F(2k_F R_m) \quad . \quad (1)$$

In this expression, Z is the number of conduction electrons per atom, g_J is the Landé g factor for the ground state of total angular momentum J, Γ is a diagonal s-f exchange integral, k_F is the Fermi momentum, and E_F is the Fermi energy. R_m is the distance between rare earths, and the function $F(x)$ is

$$F(x) = (x \cos x - \sin x)/x^4 \quad .$$

The sum $\sum_m F(X_m)$ is the only term in Eq. (1) that can change sign. For a given structure it is a function only of the number of conduction electrons Z.[3] If we assume that Z remains constant, the sum is the same for all rare-earth monophosphides.[4]

Three possible explanations for the sign change of the paramagnetic Curie temperatures suggest themselves. They are (i) the crystal field spuriously contributes to the Θ_p; (ii) the sum $\sum_m F(X_m)$ varies in such a way as to fit the observed data; and (iii) the RKKY interaction is insufficient. Other terms are present in the indirect-exchange interaction. A plot of the inverse susceptibility of paramagnetic ions subject to crystal fields appears linear over a wide range of temperatures