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Effect of Environmental Nuclei in Electron Spin Resonance Spectroscopy*

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Occasionally an electron paramagnetic resonance absorption line is accompanied by satellite lines which result from a weak magnetic dipole-dipole interaction coupling the electron spin to a neighboring nuclear spin. The satellites correspond to a change in spin state of the neighbor nucleus concurrent with the change in spin state of the electron. Expressions for the energy levels and transition probabilities for a spin-only electron coupled to neighboring nuclei are given. An example of atomic hydrogen in a glassy solid coupled to nearby protons is treated, and some of the more general consequences of the interaction are pointed out.

INTRODUCTION

IN an earlier, preliminary report[1] attention was called to extra satellite absorption lines that appear in the paramagnetic resonance spectrum for atomic hydrogen produced in various acids at a low temperature by irradiation with gamma rays. Each of the two atomic hydrogen hyperfine lines had a pair of satellite lines. The frequency spacing from satellite to main line in each case was close to the appropriate proton magnetic resonance frequency for the applied field of 3000 or 8000 gauss. The ratio of the satellite to main-line intensity varied approximately as the inverse square of the applied field strength. These observations were interpreted as the occasional concurrent spin flip of the electron and a nearby proton because of their magnetic dipole-dipole coupling. By using transition probabilities derived from this interpretation, under certain simplifying assumptions it was possible to compute an effective distance of the atomic hydrogen to its neighboring proton(s), and a preliminary value for this distance, 1.8 A assuming a single near-neighbor proton, was reported.

The appearance of such satellite lines is not restricted to atomic hydrogen in the presence of nearby protons, and in this paper formulas are given for the spacing and intensities of satellites in terms of the probability distribution function of the unpaired electron and the spins and positions of the surrounding nuclei. For simplicity, the interaction of the electron with the applied field is assumed to be much stronger than interactions involving nuclei, the orbital angular momentum of the electron is assumed to be either zero or completely quenched, internuclear dipole-dipole interactions are neglected, and quadrupole forces on the nuclei are also neglected. The derived formulas are then applied to the case of atomic hydrogen.

THEORY

The appropriate spin-dependent part of the Hamiltonian is

$$\mathcal{H}=-\boldsymbol{\mu}_e\cdot\mathbf{H}-\textstyle\sum_i(\mathbf{H}+\mathbf{h}_{ei})\cdot\boldsymbol{\mu}_i, \tag{1a}$$

where e and i refer to electron and nuclei, respectively, $\boldsymbol{\mu}$ is the magnetic moment operator, $\mathbf{H}$ is the applied field (taken in the z direction), and $\mathbf{h}_{ei}$ is the field of the electron at the ith nucleus. More explicitly, the Hamiltonian may be written as

$$\mathcal{H}=-g_e\beta_eS_{ez}H-\sum_i g_i\beta_NS_{iz}H-\sum_i g_e\beta_e\left\{\frac{8\pi}{3}\mathbf{S}_e\delta(r_{ei})-\frac{1}{r_{ei}^3}\left[\mathbf{S}_e-\frac{3(\mathbf{S}_e\cdot\mathbf{r}_{ei})\mathbf{r}_{ei}}{r_{ei}^2}\right]\right\}\cdot g_i\beta_N\mathbf{S}_i, \tag{1b}$$

where g is the gyromagnetic ratio, β_e and β_N the Bohr and nuclear magneton, $\mathbf{S}$ the spin operator in units of $\hbar$, and $\mathbf{r}_{ei}$ the vector joining the electron and ith nucleus.

For the type of system being considered, we have $\boldsymbol{\mu}_e\cdot\mathbf{H}\gg\boldsymbol{\mu}_i\cdot(\mathbf{H}+\mathbf{h}_{ei})$, and thus the eigenstates and eigenvalues of $\mathcal{H}$ differ by only small amounts from those of $\mathcal{H}_0=-\boldsymbol{\mu}_e\cdot\mathbf{H}$ and may be well approximated by first order perturbations. Since complete quenching has been assumed, the zero-order state vector may then be represented by

$$|U_0)\equiv|a;M_e;\boldsymbol{\tau}_i(M_e),M_i), \tag{2}$$

where a represents the quantum numbers which serve to fix the spatial distribution of the electron and where

$$\boldsymbol{\tau}_i(M_e)\equiv\frac{\mathbf{h}_{ei}(M_e)+\mathbf{H}}{|\mathbf{h}_{ei}(M_e)+\mathbf{H}|}, \tag{3}$$

$$S_{ez}|U_0)=M_e|U_0),\quad M_e=\pm\tfrac{1}{2}, \tag{4}$$

$$\mathbf{S}_i\cdot\boldsymbol{\tau}_i|U_0)=M_i|U_0),\quad M_i=S_i,\quad S_i-1,\cdots,-S_i, \tag{5}$$

$$\mathbf{h}_{ei}(M_e)=M_eg_e\beta_e\left\{\frac{8\pi}{3}|\psi(\mathbf{r}_e)_i|^2\boldsymbol{\tau}_z-\left\langle\frac{1}{r_{ei}^3}\left(\boldsymbol{\tau}_z-\frac{3z_{ei}\mathbf{r}_{ei}}{r_{ei}^2}\right)\right\rangle\right\}. \tag{6}$$

Here $\mathbf{h}_{ei}(M_e)$ is the magnetic field of the electron, in state M_e, at the ith nucleus; $\psi(\mathbf{r}_e)_i$ is the electron wave function evaluated at the ith nucleus; and the angular brackets, $\langle\ \rangle$, indicate the expectation value is taken

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[1] H. Zeldes and R. Livingston, Phys. Rev. 96, 1702 (1954).

for the spatial part of the wave function for the unpaired electron. Note that $\boldsymbol{\tau}_i$ is a unit vector giving the direction of the total field acting on the ith nucleus while $\boldsymbol{\tau}_z$ is a unit vector along the direction of $\mathbf{H}$. The magnetic fields at a nucleus are indicated vectorially in Fig. 1 for the two states of the electron (M_e and M_e').

The zero-order state vectors [Eq. (2)] have the property that among states with the same value of M_e, $\mathcal{H}$ is diagonal, and its diagonal elements, the energy eigenvalues to first order, are

$$E(M_e,M_i)=-g_e\beta_eM_eH-\textstyle\sum_i g_i\beta_NM_i|\mathbf{H}+\mathbf{h}_{ei}(M_e)|. \quad (7)$$

These zero-order states are states of good M_e and M_i. The effect of the first-order correction will be to admix states of different M_e and M_i. A zero-order state of given M_e ($\pm\frac{1}{2}$) will have added to it states with the opposite M_e with weight approximately $\sum_i \mathbf{h}_{ei}\cdot\boldsymbol{\mu}_i/(\mathbf{H}\cdot\boldsymbol{\mu}_e)$. For simplicity this admixture has been neglected in this paper. As indicated later, this restriction leads to negligible error for atomic hydrogen for fields in excess of, say, 3000 gauss.

If an oscillating field of the proper frequency is applied to a sample containing some unpaired electrons, transitions are induced between the levels with energies given by (7). The transition probabilities between levels of the same M_e but with one M_i differing by one unit are proportional to $g_i^2\beta_N^2[H_\omega(\perp\boldsymbol{\tau}_i)]^2$, where $H_\omega(\perp\boldsymbol{\tau}_i)$ is the component of the oscillating field which is perpendicular to $\boldsymbol{\tau}_i$ [Eq. (3)]. In general $\boldsymbol{\tau}_i$ is not in the direction of $\mathbf{H}$ (the z direction) and transitions can be induced by an oscillating field along $\mathbf{H}$. The transitions observed in electron spin resonance are for levels of different M_e. Here the transition probabilities are proportional to $g_e^2\beta_e^2[H_\omega(\perp\mathbf{H})]^2$, where $H_\omega(\perp\mathbf{H})$ is the component of the oscillating field perpendicular to $\mathbf{H}$. When the transition is made each $\boldsymbol{\tau}_i$, in general, changes direction according to Eqs. (3) and (6) (see Fig. 1). This change in the direction of quantization for $\mathbf{S}_i$ permits changes in M_i to occur. In particular the transition probability from state $|M_e,M_i)$ to $|M_e',M_i')$, where M_e' is different from M_e, is given by

$$T(M_e',M_i';M_e,M_i)$$

$$=\frac{g_e^2\beta_e^2[H_\omega(\perp\mathbf{H})]^2}{4\omega\hbar^2}\prod_i|D_{M_iM_i'}{}^{S_i}(\beta_i)|^2, \quad (8)$$

where D^{S_i} is the rotation matrix[2] for a particle of spin S_i, β_i is the angle between $\boldsymbol{\tau}_i(M_e)$ and $\boldsymbol{\tau}_i(M_e')$, and $2H_\omega(\perp\mathbf{H})$ is the strength of the sinusoidal magnetic field perpendicular to $\mathbf{H}$ and oscillating at angular frequency ω.

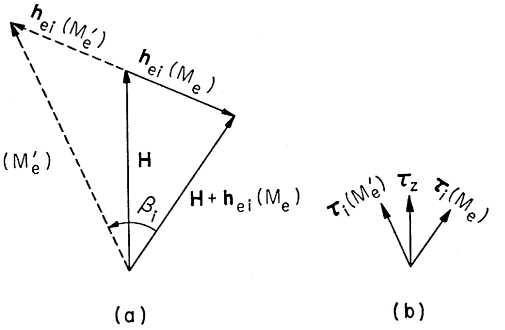

FIG. 1. (a) The magnetic fields at a nucleus for the two states of the electron. The symbols are defined in the text. (b) The corresponding unit vectors.

In terms of the fields (see Fig. 1),

$$\cos\beta_i=\frac{H^2-h_{ei}^2}{[(H^2-h_{ei}^2)^2+4h_{i\perp}^2H^2]^{\frac{1}{2}}}, \quad (9)$$

where $h_{i\perp}$ is the component of $\mathbf{h}_{ei}$ perpendicular to $\mathbf{H}$. For $|2h_{i\perp}H/(H^2-h_{ei}^2)|$ small, then

$$\beta_i\approx\left|\frac{2h_{i\perp}H}{H^2-h_{ei}^2}\right| \quad \text{if} \quad h_{ei}<H, \quad (10)$$

and

$$\pi-\beta_i\approx\left|\frac{2h_{i\perp}H}{H^2-h_{ei}^2}\right| \quad \text{if} \quad h_{ei}>H. \quad (11)$$

Then for β_i small,

$$D_{MM'}{}^S\propto\beta_i{}^{|M-M'|}=\left|\frac{2h_{i\perp}H}{H^2-h_{ei}^2}\right|^{|M-M'|}, \quad (12)$$

and for $(\pi-\beta_i)$ small,

$$D_{MM'}{}^S\propto(\pi-\beta_i)^{|M+M'|}=\left|\frac{2h_{i\perp}H}{H^2-h_{ei}^2}\right|^{|M+M'|}. \quad (13)$$

If β_i is small for a particular nucleus, then according to Eqs. (8), (10), and (12) the most prominent transitions are ones in which $\Delta M=0$ for the nucleus. Transitions for which $\Delta M\neq 0$ will be reduced in intensity by a factor $\beta^{2|\Delta M|}$. According to Eq. (10), for β_i to be small it is necessary for h_{ei} to be less than H; it is sufficient for h_{ei} to be small compared to H, but not necessary since $h_{i\perp}$ may be small. This situation will be realized for nuclei sufficiently far from the electron. Similarly, if β_i is near π for a particular nucleus, then according to Eqs. (8), (11), and (13) the most prominent transitions are ones in which $M=-M'$ where the corresponding directions of quantization are essentially $\boldsymbol{\tau}_i$ and $\boldsymbol{\tau}_i'=-\boldsymbol{\tau}_i$. This would correspond to the usual $\Delta M_i=0$ transitions where the axis of quantization is fixed in space. Transitions for which M is not equal to $-M'$ will be reduced in intensity by a factor $(\pi-\beta)^{2|M+M'|}$. It is necessary now for h_{ei} to be greater than H; it is sufficient for h_{ei} to be large compared to H, but again not necessary, since $h_{i\perp}$ may be small compared to H. This situation is often realized when the electron spends considerable time on the atom of the nucleus. If β_i is

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[2] See, for example, M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley and Sons, Inc., New York, 1957), pp. 62, 73.

not near zero nor π, then the full expression for the D matrix must be used, and transitions involving any ΔM may occur with appreciable probability.

The components of h_{ei} [Eq. (6)] are given by

$$h_{i\parallel}=\frac{8\pi}{3}M_e g_e \beta_e |\psi(\mathbf{r}_e)_i|^2 - M_e g_e \beta_e \left\langle \frac{1}{r_i^3}(1-3\cos^2\theta_i)\right\rangle$$

$$h_{i\perp}=3M_e g_e \beta_e \left| \left\langle \frac{1}{r_i^3}\sin\theta_i \cos\theta_i e^{i\phi_i}\right\rangle \right|, \tag{14}$$

where r_i, θ_i, ϕ_i are polar coordinates of the electron with respect to the ith nucleus with the applied field as the polar axis. Or, alternatively,

$$\mathbf{h}_{ei}(\mathbf{r}_i)=M_e g_e \beta_e \left\{ \frac{8\pi}{3}|\psi(\mathbf{r}_e)_i|^2 \boldsymbol{\tau}_z + \boldsymbol{\tau}_z \cdot (\nabla\nabla)\phi(\mathbf{r}) \right\}_{\mathbf{r}=\mathbf{r}_i}, \tag{15}$$

where

$$\phi(\mathbf{r})=\int_\epsilon^\infty \frac{\rho(\mathbf{r}_e)}{|\mathbf{r}-\mathbf{r}_e|}d^3r_e, \quad \rho(\mathbf{r}_e)\equiv|\psi(\mathbf{r}_e)|^2. \tag{16}$$

In (16) the ϵ indicates that a small spherical region surrounding $\mathbf{r}_e=\mathbf{r}$ is excluded in computing $\phi(\mathbf{r})$ and its derivatives, and then the limit as $\epsilon \rightarrow 0$ is taken. The problem in calculating $\mathbf{h}_{ei}$ then involves that of calculating the electrostatic potential ϕ contributed by the unpaired electron. The first term in (15) is isotropic whereas the second term is anisotropic and depends upon the symmetric tensor, with zero trace, $[\nabla\nabla\phi]_{\mathbf{r}=\mathbf{r}_i}$.

If the unpaired electron is concentrated on a single atom or if it is distributed over several atoms but with negligible probability of being found between them (overlap region), then $\rho(\mathbf{r}_e)$ may be written

$$\rho(\mathbf{r}_e)=\textstyle\sum_j \rho_j(\mathbf{r}_e-\mathbf{r}_j), \tag{17}$$

where ρ_j is obtained from simple atomic orbitals centered at the jth site. This leads to simplifications in the calculation of $\mathbf{h}_{ei}$ from Eq. (15). Of course $\rho(\mathbf{r}_e)$ may be written in the form of Eq. (17) in any case, but only if there is negligible overlap are the ρ_j's expressible in terms of a few simple atomic orbitals. By using (17) and (16), ϕ at (or near) the site of the ith nucleus may be written

$$\begin{aligned}\phi(\mathbf{r}_i)=&\sum_{l,m}\sum_{j\neq i}\frac{Y_{lm}(\theta_{ij},\phi_{ij})}{(2l+1)r_{ij}^{l+1}}\int_0^\infty 4\pi r_{ej}^{l+2}\\ &\times Y_{l,m}^*(\theta_{ej},\phi_{ej})\rho_j(\theta_{ej},\phi_{ej},r_{ej})d\Omega_{ej}dr_{ej}\\ &+\sum_{l,m}\frac{r_{ii}^l Y_{l,m}(\theta_{ii},\phi_{ii})}{2l+1}\int_\epsilon^\infty \frac{4\pi}{r_{ei}^{l+1}}\\ &\times Y_{l,m}^*(\theta_{ei},\phi_{ei})\rho_i(\theta_{ei},\phi_{ei},r_{ei})d\Omega_{ei}dr_{ei}.\end{aligned} \tag{18}$$

Here $(r_{ij},\theta_{ij},\phi_{ij})$ and $(r_{ii},\theta_{ii},\phi_{ii})$ are polar coordinates giving the location of the point described by $\mathbf{r}_i$ with respect to nuclei j and i, respectively. Polar coordinates $(r_{ej},\theta_{ej},\phi_{ej})$ and $(r_{ei},\theta_{ei},\phi_{ei})$ describe the atomic orbitals centered on the nuclei j and i. After the differentiations indicated by $\nabla\nabla\phi$ are performed, r_{ii} is allowed to go to zero.

As an example, the contribution of the jth atom to the potential at the ith nucleus under the assumption that the jth orbital is a hybridized S-P orbital is

$$\begin{aligned}\phi_j(\mathbf{r}_i)=&\frac{(a_S^{(j)})^2+(a_P^{(j)})^2}{r_{ij}}-\frac{2}{\sqrt{3}}\left(\boldsymbol{\tau}_p\cdot\nabla_i\frac{1}{r_{ij}}\right)a_S^{(j)}a_P^{(j)}\\ &\times\int_0^\infty f_S(r_{ej})f_P(r_{ej})r_{ej}(4\pi r_{ej}^2)dr_{ej}\\ &+\frac{1}{5}\left[(\boldsymbol{\tau}_P\cdot\nabla_i)^2\frac{1}{r_{ij}}\right](a_P^{(j)})^2\\ &\qquad\times\int_0^\infty f_P^2(r_{ej})r_{ej}^2(4\pi r_{ej}^2)dr_{ej}\\ =&\frac{1}{r_{ij}}\int_0^\infty \rho_j(\mathbf{r}_{ej})d^3r_{ej}-\left(\boldsymbol{\tau}_P\cdot\nabla_i\frac{1}{r_{ij}}\right)\\ &\times\int_0^\infty \rho_j(\mathbf{r}_{ej})\boldsymbol{\tau}_P\cdot\mathbf{r}_{ej}d^3r_{ej}+\frac{1}{4}\left[(\boldsymbol{\tau}_P\cdot\nabla_i)^2\frac{1}{r_{ij}}\right]\\ &\qquad\times\int_0^\infty \rho_j(\mathbf{r}_{ej})[3(\boldsymbol{\tau}_P\cdot\mathbf{r}_{ej})^2-r_{ej}^2]d^3r_{ej}.\end{aligned} \tag{19}$$

The $|a|^2$'s give the probability of the electron being in the S or P states of the jth atom, the f's are the radial wave functions, and $\boldsymbol{\tau}_P$ is the direction of the quenched P orbital. The dipole and quadrupole terms (absent for a pure S state) are of the order of (the atomic radius $\div r_{ij}$) to the first and second power, respectively, times the monopole term, and although they may be important for nearby atoms, for simplicity of discussion we shall assume they may be ignored. With this assumption, the field at the ith nucleus is

$$\begin{aligned}\mathbf{h}_{ei}=M_e g_e \beta_e\Bigg\{&\sum_j \frac{(a^{(j)})^2}{r_{ij}^3}\left(\frac{3(\mathbf{r}_{ij}\cdot\boldsymbol{\tau}_z)\mathbf{r}_{ij}}{r_{ij}^2}-\boldsymbol{\tau}_z\right)\\ &+\boldsymbol{\tau}_z(a_S^{(i)})^2(8\pi/3)[f_S^{(i)}(0)]^2\\ &+(3\boldsymbol{\tau}_P^{(i)}\cdot\boldsymbol{\tau}_z\boldsymbol{\tau}_P-\boldsymbol{\tau}_z)(a_P^{(i)})^2(\tfrac{2}{5})\\ &\times\int_0^\infty [f_P^{(i)}(r_{ei})]^2(1/r_{ei}^3)(4\pi r_{ei}^2)dr_{ei}\Bigg\}.\end{aligned} \tag{20}$$

In the above equation, the contributions of S and P orbitals on the ith nucleus have been included. Usually

$[f_S^{(i)}(0)]^2$ is so large (and often $\langle 1/r^3\rangle$ for P electrons is sufficiently large) that if $(a^{(i)})^2$ is greater than a few percent, the contribution to $\mathbf{h}_{ei}$ from atoms other than i is negligible and moreover $h_{ei} \gg H$. According to Eq. (11) $\pi-\beta_1$ would be near zero. If in addition $(a_S^{(i)})^2$ is appreciable compared to $(a_P^{(i)})^2$, then $h_{i\perp}$ will be small compared to h_{ei}, which will cause a further reduction in the value of $\pi-\beta_i$. Therefore the spin of such a nucleus will not reorient when the electron does, and only the normal hyperfine spectrum will be seen. Those nuclei which do not share the electron (or which have it only a small portion of the time) will have an h_{ei} not very large compared to typical laboratory fields (say, 10 000 gauss), and may have an appreciable value for $Hh_{i\perp}/(H^2-h_{ei}^2)$. Such nuclei will contribute extra lines to the electron-spin resonance spectrum corresponding to changes in spin orientation of these neighboring nuclei during the electron transition. These lines are what are here referred to as the satellite lines, and if h_{ei} is small compared to H they will be equally spaced about the usual hyperfine lines with a spacing $g_N\beta_N H$. Of course, if β_i or $(\pi-\beta_i)$ is not small, the $M=M'$ or the $M=-M'$ transitions are not favored, and the distinction between "main" and "satellite" lines loses significance.

EXAMPLE OF ATOMIC HYDROGEN NEAR A PROTON

The atomic hydrogen spectrum in low-temperature gamma-irradiated sulfuric acid (5 moles of water to one of acid quick-frozen to a glass), as described earlier,[1] consists of the two atomic hydrogen hyperfine lines, each flanked by a pair of satellites spaced from the central line by nearly the proton magnetic-resonance energy. At the concentration of acid used,[3] the atomic hydrogen hyperfine interaction is within 1% of the free-atom value. Moreover there are no additional lines centering at $g_e=2$. These observations indicate that the electron is concentrated on a single proton. For atomic hydrogen near a neighboring proton, consideration must be given to the additional interaction of the electron with the atomic hydrogen nucleus. The energy of this interaction amounts to 1420 Mc/sec (or 505 gauss for the electron transition), and is exceeded only by the strength of the interaction of the electron with the applied field (several thousand gauss). Calculations have been made that show that the error in ignoring the effect of the atomic hydrogen hyperfine interaction on the satellite transition rate is negligible for strong fields, say in excess of 8000 gauss, while with fields of about 3000 gauss errors of about 10% in the transition rates (or 1.7% in distance) would be incurred. The treatment given here is for measurements made at 7982 gauss and will ignore the hyperfine interaction.

If Eq. (20) is specialized to the case of the unpaired electron concentrated on a single atom, then

$$\mathbf{h}_{ei}=M_e g_e \beta_e \frac{1}{r_i^3}\left[\frac{3(\mathbf{r}_i\cdot\boldsymbol{\tau}_z)\mathbf{r}_i}{r_i^2}-\boldsymbol{\tau}_z\right]; \tag{21}$$

or

$$h_{ei}^2=M_e^2 g_e^2 \beta_e^2 \frac{1}{r_i^6}[(1-3\cos^2\theta_i)^2+9\cos^2\theta_i \sin^2\theta_i],$$

$$h_{i\perp}=M_e g_e \beta_e \frac{1}{r_i^3}(3\cos\theta_i \sin\theta_i), \tag{22}$$

$$h_{i\parallel}=M_e g_e \beta_e \frac{1}{r_i^3}(3\cos^2\theta_i-1),$$

where $\mathbf{r}_i$ is the vector distance between the ith nucleus and the nucleus of the atom containing the unpaired electron, and θ_i is the angle between this vector and $\mathbf{H}$. Experimental observations in strong applied fields show the satellites to be relatively weak and narrow compared to their spacing and hence h_{ei}/H is small. Since the only magnetic nuclei in the system are protons, the appropriate rotation matrix is

$$D^{(1/2)}=\begin{pmatrix}\cos(\beta/2) & -\sin(\beta/2)\\ \sin(\beta/2) & \cos(\beta/2)\end{pmatrix}. \tag{23}$$

Since h_{ei} is small, the satellites will be spaced [Eq. (7)] at $\pm g_i\beta_N H$ from a central (unresolved) line at $g_e\beta_e H$.

Now from Eqs. (8), (10), (22), and (23),

$$\frac{T_1}{2T_2}\approx\frac{9}{8}\sum_i \frac{g_e^2\beta_e^2}{H^2 r_i^6}\sin^2\theta_i \cos^2\theta_i, \tag{24}$$

where the ratio of intensity of either satellite line, T_1, to that of the two superimposed central lines, $2T_2$, is given. For a large number of randomly oriented systems, such as would be found on measurements of polycrystalline or glassy materials, (24) gives

$$\frac{\bar{T}_1}{2\bar{T}_2}\approx\frac{3}{20}\left\langle\sum_i \frac{g_e^2\beta_e^2}{H^2 r_i^6}\right\rangle. \tag{25}$$

Here the average indicated by the angular brackets $\langle\ \rangle$ provides for the possibility that different hydrogen atoms have different environments.

The experimentally measured ratio $\bar{T}_1/2\bar{T}_2$ was 0.030 with an applied magnetic field of 7982 gauss. With a defined effective single-proton distance given by

$$r_{\text{eff}}\equiv\left[\left\langle\sum_i \frac{1}{r_i^6}\right\rangle\right]^{-1/6}, \tag{26}$$

the calculated value is $r_{\text{eff}}=1.73$ A. This value is slightly smaller than the preliminary value of 1.80 A reported[1] earlier. If each hydrogen atom had n nearby protons at the same distance, this distance would be

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[3] Livingston, Zeldes, and Taylor, Discussions Faraday Soc. **19**, 166 (1955).

$n^{1/6}r_{\mathrm{eff}}$. It is likely, however, that in the glassy materials used the nearby proton environments of all the hydrogen atoms were not the same. Hence an interpretation of r_{eff} in terms of actual distances would depend upon the assumed nature of the distribution. It should be noted that the satellite intensity, being proportional to $1/r^6$, is relatively insensitive to all but the nearest protons. If observations were made with a spectrometer of sufficient sensitivity, a second set of satellites ($1/r^{12}$ intensity dependence) could be observed corresponding to two neighboring protons concurrently changing state. Such observations would give additional information on the nature of this proton distribution.

Satellite lines have been seen in systems other than those containing atomic hydrogen. In gamma-irradiated materials at low temperatures, the paramagnetic-resonance lines are often sufficiently sharp that the satellites from environmental protons are completely resolved at 8000 gauss, but they are often weak compared to the central line. At 3000 gauss they are much stronger because of the $1/H^2$ dependence, but are often not clearly resolved. For the cases discussed here an intermediate field would be optimum. The transition probabilities can be appreciable for distances out to, say, 3 A. The satellite intensity does not depend upon the magnetic moment of the neighbor nucleus, but if the moment is small the satellites may not be resolved. They will however contribute to the width of the main absorption line. Van Vleck[4] purposely discarded terms giving rise to satellites in his second-moment development, and accordingly, if a moment analysis of a paramagnetic-resonance line is made, care should be taken to exclude the effect of satellite lines.

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[4] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

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Magnetic Susceptibility of a Sintered Rod of αMnS†

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The magnetic susceptibility of a sintered sample of αMnS was measured from 90°K to 550°K by an absolute Gouy method. The extrapolated susceptibility at 0°K was approximately equal to 7/10 the maximum susceptibility at the Néel point (154°K). It was not possible to fit the data above the Néel point with a unique set of Weiss-Curie constants, probably due to the persistence of short-range ordering effects above the Néel temperature. Upon using the recent Wojtowicz application of the Ising-Bethe theory, a unique set of constants, $\mathcal{J}/k=-100.5$°K and $C_M=3.57$, fitted the data satisfactorily between 175°K and 550°K. A diamagnetic correction of 58×10^{-6} per mole was applied to the data before calculating the above values. Above the Néel point the susceptibility of the sintered specimen was less than the susceptibility of a powder sample by a factor which was too large to be explained in terms of the standard correction for powders or by differences in geometry. Multiple maxima in the susceptibility which were outside the range of experimental error were noted at 144°K, 151°K, 157°K, and 167°K. When considered in conjunction with the specific heat anomalies previously detected at 139°K and 147°K, it is suggested that a change in either spin ordering or crystal structure occurs in this temperature region and is responsible for the irregular susceptibility behavior.

INTRODUCTION

THE magnetic susceptibility of αMnS powder has previously been reported by the authors.[1] These data showed a Néel temperature of 154°K and a rather broad plateau of susceptibility between 154°K and 170°K, and indicated that a single set of Weiss-Curie constants would not fit the curve up to 800°K. It was felt that there might be some interest in a study of the sintered type of sample with the same composition and structure.

EXPERIMENTAL

The αMnS powder[1] was prepared for sintering by being mixed with distilled water and then extruded as a paste into a long cylindrical rod. After initial drying at 100°C, the rod was sintered in a vacuum of about 10^{-4} mm for two hours at 1150°C. The result was a hard green-grey specimen with a slight metallic luster. Chemical analysis indicated the final composition to be better than 99% MnS. X-ray analysis showed the structure to be NaCl type with a lattice constant of 5.20 A, the same as the powder sample. The sample had an average diameter of 0.41 cm and a length of 10.0 cm. Its measured density was 2.6 g/cm^3 which is 65% of the crystalline density of 3.99 g/cm^3. The

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[1] J. J. Banewicz and R. Lindsay, Phys. Rev. 104, 318 (1956).