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Hyperfine resonance properties of Er^{3+} in Au[†]

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The direct hyperfine resonance spectra of the Γ_7 ground state of isotopically enriched ^{167}Er^{3+} in a dilute Au matrix have been measured in the millikelvin temperature region at frequencies of 230–300 MHz. The spectra were fitted to an isotropic spin Hamiltonian with the magnetic hyperfine constant A and the pseudonuclear g factor g_n' as fitting parameters. Knowledge of g_n' makes it possible to estimate the energy separation Δ of the first-excited $\Gamma_8^{(1)}$ quartet from the ground state. This separation was found to be 11 ± 2 K which is in fair agreement with reported measurements at X band, where $\Delta = 16 \pm 6$ K. The hyperfine constant A deduced from the rf spectrum is negative and $|A|$ is approximately 2% smaller than the A value derived from the X-band spectrum. The linewidth is of the form $a(H) + bT$, where $b = 13$ G/K and the residual linewidth $a(H)$ is a function of magnetic field.

INTRODUCTION

For reasons related to the development of a magnetic-resonance thermometer in the millikelvin temperature region, we have studied the resonance properties of the rare-earth ion Er^{3+} imbedded in an Au matrix at low temperatures. Previous work on Er in a dielectric with the same local symmetry (ThO$_2$: Er)[1] suggested that the rare-earth–metal system might be applicable for low-temperature thermometry.

The success of the observation of crystal-field effects in the microwave EPR of rare-earth ions in dilute alloys has also contributed to further resonance studies of these systems. The microwave spectra of Er in Au and several other metals[2] have been resolved and from the temperature dependence of the EPR linewidth and from the g shift, the effect on the ground state from higher-lying crystal-field states can be deduced.[3] In the present work, we report observations of the "direct hyperfine transitions" within one multiplet of ^{167}Er ($S=\frac{1}{2}$, $I=\frac{7}{2}$) in a dilute Au-based alloy. These resonances occur at magnetic fields of the order of 100–400 G at 200–300 MHz. The hyperfine coupling constant A and the pseudonuclear g factor g_n' can be derived from the spectrum. The influence of excited crystal-field states on the ground state is reflected in g_n' and knowledge of the latter allows a determination of the energy separation Δ between the Γ_7 ground doublet and the first-excited $\Gamma_8^{(1)}$ quartet. We obtain a value of Δ which is in fair agreement with values deduced from EPR linewidth measurements.[3] The hyperfine constant A derived from the rf spectrum is negative and $|A|$ is slightly smaller than $|A|$ deduced from high-field microwave measurements.[2]

The direct hyperfine spectrum was resolved at temperatures less than a few tenths of a degree K. The temperature dependence of the linewidth appears to be approximately linear, characteristic of relaxation via conduction-electron spins. The linewidth is also a strong function of magnetic field.

TRIVALENT ERBIUM IN A CUBIC FIELD

The Er^{3+} free ion ($4f^{11}$) has a $J=\frac{15}{2}$ multiplet ground state which in a cubic crystal field is split into three Γ_8 quartets, one Γ_6 doublet, and one Γ_7 doublet. The separation of the energy levels has been calculated (within a multiplicative factor) by Lea, Leask, and Wolf[4] and the relative positions of the levels are a function of two parameters, the fourth- and sixth-order terms of the cubic potential. Static susceptibility[5] and paramagnetic resonance[6] have been interpreted in terms of a crystal-field ground Γ_7 doublet with a $\Gamma_8^{(1)}$ quartet as the first-excited state. The appropriate isotropic spin Hamiltonian describing the ground-state doublet is

$$\mathcal{H} = g\mu_B \vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S} - g_n'\mu_N \vec{H}\cdot\vec{I}\,, \qquad (1)$$

where the first and third terms, respectively, are electronic and nuclear Zeeman energies and the second term represents the hyperfine interaction energy. For an isolated doublet, S has the value $\frac{1}{2}$ and the nuclear spin I for ^{167}Er is $\frac{7}{2}$. The eigenvalues of the above spin Hamiltonian are given by the Breit-Rabi formula

$$\begin{aligned} E(F, m_F) = &-\tfrac{1}{4}A - g_n'\mu_N H m_F \\ &+ \tfrac{1}{2}A(2I+1)(F-I)[1 - 2\delta_{m_F,p}\Theta(x)] \\ &\times\left(1 + \frac{4m_F}{2I+1}x + x^2\right)^{1/2}, \end{aligned} \qquad (2)$$

where

$$\vec{F} = \vec{S} + \vec{I}, \quad m_F = M + m,$$

$$\delta_{m_F,p} = \begin{cases} 1 \text{ if } m_F = p \\ 0 \text{ if } m_F \neq p \end{cases},$$

$$x = \frac{g\mu_B + g_n'\mu_N}{\frac{1}{2}A(2I+1)} H\,,$$

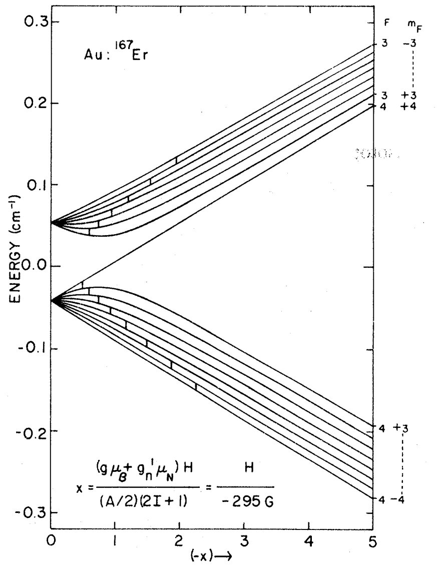

FIG. 1. Γ_7 ground-state energy levels of ^{167}Er^{3+} in Au as a function of magnetic field. Direct hyperfine transitions at 250 MHz are indicated with veritcal lines.

$$\Theta(x) = \begin{cases} 0 \text{ for } |x| < 1 \\ 1 \text{ for } |x| > 1 \end{cases}$$

$$p = -(I + \tfrac{1}{2})Ag/|Ag| \; .$$

For $S = \frac{1}{2}$ and $I = \frac{7}{2}$, there are two hyperfine multiplets, $F = 3, 4$ and the sign of A determines which one is the ground multiplet. In Fig. 1 the ground-state energy levels of Au: Er are shown as a function of magnetic field. The vertical lines indicate the direct hyperfine transitions $\Delta F = 0$ and $\Delta m_F = \pm 1$ at a frequency of 250 MHz. The dependence of the resonance frequencies on magnetic field is given by

$$h\nu = E(F, m_F + 1) - E(F, m_F) \; . \tag{3}$$

It should be emphasized that the low-field rf transitions we are discussing are actually dominated by electron transitions and not by nuclear transitions. This can be understood by recognizing that the eigenstates of (1) are not simple (electron spin)×(nuclear spin) product states when the nondiagonal part of the hyperfine term is retained, but the eigenstates are linear combinations of product states from each multiplet. Hence, the rf transition probability will contain both an electronic and nuclear driving term, and for weak magnetic fields (~100 G) the electronic term is much larger.

EXPERIMENTAL PROCEDURE

A powdered Au sample[7] containing nominally 100-ppm isotopically enriched ^{167}Er was contained in the mixing chamber of a dilution refrigerator. The particle size was approximately 100 μm. Resonance data were taken over the temperature range 0.040–0.3 K and at 230, 250, and 300 MHz on a cw spectrometer which has been described in detail elsewhere.[8]

EXPERIMENTAL RESULTS

The derivative of the direct hyperfine spectrum of 100-ppm ^{167}Er in Au is shown in Figs. 2(a) and 2(b). This spectrum was taken at 40–45 mK at a rf frequency of 250 MHz. Spectra taken at 230 and 300 MHz exhibited essentially the same features. The numbers within parenthesis in Fig. 2 state the appropriate $m_F \leftrightarrow m_F'$ for each hyperfine transition and we note that all eight transitions of the lower multiplet ($F = 4$) have been resolved.[9] The shape of the lines is Dysonian[10] which is characteristic of the magnetic resonance of localized moments in a metal matrix with particle size larger than the skin depth. The ratio of the derivative peak heights

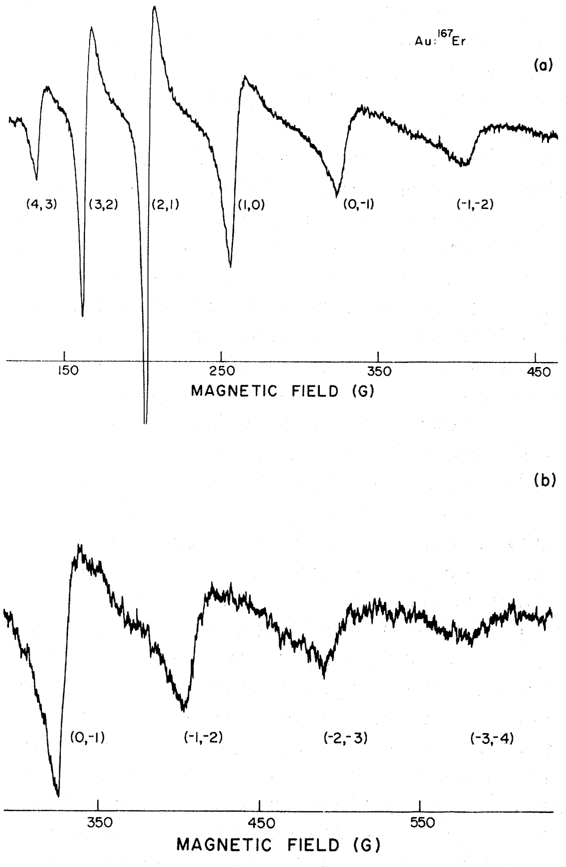

FIG. 2. (a) Direct hyperfine resonance spectrum (derivative of the absorption) for a powdered sample of 100-ppm ^{167}Er in Au at 40–45 mK at 250 MHz for magnetic fields up to 450 G. The numbers within parenthesis indicate the appropriate $m_F \leftrightarrow m_F'$ for each individual transition. (b) Resonance spectrum for magnetic fields between 300 and 650 G with vertical scale expanded by a factor of 2.5.

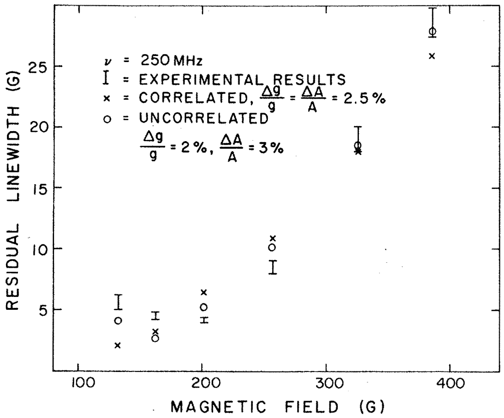

FIG. 3. Residual linewidth ΔH as a function of magnetic field for the six strongest hyperfine lines in Au : Er at about 40 mK and 250 MHz. A minimum in ΔH is observed at ~200 G [for line (2, 1)]. Also shown is the calculated linewidth when A and g are correlated and uncorrelated.

(A'/B in the notation by Feher and Kip[11]) varies between 2 and 3 and is dependent on magnetic field. The linewidth ($\frac{1}{2}A'$) of the resonance lines is not constant but increases with magnetic field. In Fig. 3 the linewidth at about 40 mK is plotted versus magnetic field for the six most intense lines and a minimum at about 200 G [for line (2, 1)] is observed. With increasing temperature, the linewidth exhibited a temperature dependence of the form $a(H)+bT$. In Fig. 4 the linewidth of line (3, 2) is shown as a function of temperature. The linewidth appears to be linear in T and the solid line fitted to the experimental points (by a least-mean-square fit) yields a slope of 13 G/K.

DISCUSSION

Crystal-field effects

The electronic g factor and the hyperfine constant A have previously been determined from microwave EPR measurements by Chock *et al.* and Tao *et al.*[2] Their measurements were conducted at 3-cm wavelength in the ^{4}He temperature range and gave a g factor of 6.80 ± 0.04 and a hyperfine constant $|A|$ of 75.0 ± 0.5 G. As g can be determined more accurately from microwave resonance than from direct hyperfine resonance, $g = 6.8$ was used and only A and g_n' were fitted to the spectra in Fig. 2. A method of linearized least-mean-square analysis[12] was used to fit Eq. (3) to the hyperfine spectrum and we found $A = -73.5 \pm 0.7$ G (-0.02330 cm^{-1}) and $g_n' = -29 \pm 2$. The uncertainties in A and g_n' are statistical and do not reflect any systematic deviations. Comparing the A values, we note that there is a small but significant difference of 1.5 G between our value and that deduced from microwave measurements.[2] This difference will be discussed in the next section.

The large value of g_n' corresponds approximately to an enhancement of 185 over the nuclear g factor of the free Er atom, $g_n = -0.1613$.[13] The enhanced nuclear g value can be understood by considering the mixing in second-order perturbation of the Γ_7 ground doublet and the higher-lying $\Gamma_8^{(1)}$ quartet states by the hyperfine interaction. The full perturbing Hamiltonian acting on the spectroscopic ground term is

$$\mathcal{H} = g_\Lambda \mu_B \vec{H} \cdot \vec{J} + a\vec{I} \cdot \vec{J} - g_n \mu_N \vec{H} \cdot \vec{I} , \tag{4}$$

where g_Λ is the Landé g factor ($=\frac{6}{5}$ for Er^{3+}). The correction to second order is of the form

$$\mathcal{H}' = \sum_f \frac{2\langle i \mid \mu_B g_\Lambda \vec{H} \cdot \vec{J} \mid f \rangle \langle f \mid a\vec{I} \cdot \vec{J} \mid i \rangle}{E_i - E_f} , \tag{5}$$

where E_i and E_f are, respectively, the energies of the ground state and the excited states. It can be shown in detail[14] that the above correction can be written for $\vec{H}$ parallel to the z axis and for a particular M_J as

$$-g_n' \mu_N H_z I_z \tag{6}$$

and where

$$g_n' = \frac{2ag_\Lambda}{E(\Gamma_8^{(1)}) - E(\Gamma_7)} \times \frac{\mu_B}{\mu_N} \sum_{M_J'} |\langle \Gamma_7, M_J | J_z | \Gamma_8^{(1)}, M_J' \rangle|^2 . \tag{7}$$

Only the mixing with the closest Γ_8 quartet has been considered. The form of the correction term (6) is that of a nuclear Zeeman interaction and can thus be included in the Hamiltonian (4) by writing the third term as $(g_n' + g_n)\mu_N \vec{H} \cdot \vec{I}$. Because crystal-field splittings in the rare earths can be quite small, the pseudonuclear g factor g_n' may be strongly enhanced over the free-ion g_n factor. The value of the matrix element in (7) depends on the ratio of the fourth- and sixth-order crystal-field coefficients and the $\Gamma_8^{(1)}$ wave functions which are tabulated in Ref. 4. The matrix element has a value between 3.28 and 3.55. Hence, one can

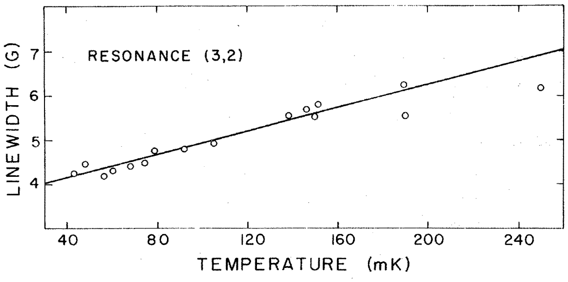

FIG. 4. Linewidth as a function of temperature for resonance line (3, 2). The slope of the straight line fitted to the experimental points is 13 ± 1 G/K.

calculate the energy separation between the Γ_7 ground state and the first-excited crystalline $\Gamma_8^{(1)}$ quartet to a precision limited by the uncertainties in g_n' and the matrix element. We find

$$E(\Gamma_8^{(1)}) - E(\Gamma_7) = 11 \pm 2 \text{ K} .$$

Crystal-field splittings of rare-earth ions in dilute noble metals were first reported by Williams and Hirst.[5] They estimated from static-susceptibility measurements on Au: Er that the first-excited Γ_8 quartet was located 19 K above the ground state. Recently, Davidov *et al.* and Rettori *et al.*[3] have estimated the energy splitting between $\Gamma_8^{(1)}$ and Γ_7 from the temperature dependence of the EPR linewidth and the g shift of the Γ_7 resonance. The closeness of the $\Gamma_8^{(1)}$ state leads to changes in the g value (as compared to that of an isolated Γ_7 doublet) and in the thermal broadening of the Γ_7 resonance. The extra structure in the broadening is a function of the temperature and is caused by additional relaxation transitions via the higher-lying Γ_8 levels; this leads to a significant deviation from the proportional-to-temperature linewidth which is usually observed when relaxation via conduction-electron spins is dominant. In Ref. 3 the Γ_7 resonance of Au: Er was measured between 1.6 and 25 K and the linewidth-temperature characteristic exhibited a sharp break in the slope at about 6 K. This break was interpreted as evidence for a nearby excited level, and from their theoretical analysis they deduce a value of 16 ± 6 K for $E(\Gamma_8^{(1)}) - E(\Gamma_7)$. Hence, the values for the energy splitting, as obtained from the two different methods, direct hyperfine resonance and microwave EPR, are in reasonable agreement considering the limited accuracy inherent in both methods, both values being somewhat smaller than the 19 K obtained from static magnetic susceptibility measurements.[5]

Linewidth

In the spectra in Fig. 2 we observe that the linewidth varies from line to line. In Fig. 3 we have plotted the linewidth versus magnetic field at about 40 mK and 250 MHz. The residual linewidth varies approximately from 4 to 30 G and exhibits a minimum for line (2, 1). At a concentration of 100-ppm Er, broadening due to interactions between the Er ions might be expected to be negligible in the absence of clustering. If the residual linewidth is due to inhomogeneous broadening resulting from dislocations, strains, etc., then the variations in the electronic g factor and the hyperfine constant should be correlated as has been demonstrated by Sroubek *et al.*[15] Since the matrix elements of the noncubic fields that admix the higher crystal-field states of the Er^{3+} ion into the Γ_7 ground state producing the variations in g and A, are exactly the same for the two parameters, we have

$$\Delta g/g = \Delta A/A . \tag{8}$$

An expression for the hyperfine linewidths in terms of the magnetic field can be derived from Eqs. (3) and (2). Under the condition that the variations in A and g are correlated as in Eq. (8) the linewidth is for $|x| < 1$

$$\frac{\Delta H}{H} = \left(\frac{x}{S}\frac{\partial S}{\partial x}\right)^{-1}\left(\frac{\Delta A}{A}\right) , \tag{9}$$

where

$$S(x) = [1 + \tfrac{1}{2}(m_F + 1)x + x^2]^{1/2} - (1 + \tfrac{1}{2} m_F x + x^2)^{1/2} .$$

$g_n'\mu_N$ is neglected in comparison to $g\mu_B$ in x. The choice of average distribution in g and A to give the best fit to the measured linewidths is $\Delta g/g = 2.5\%$ but the agreement between the calculated and observed values is not especially good. In particular, the calculated values do not show a minimum in the linewidth at the (3, 2) and (2, 1) resonances as observed experimentally, see Fig. 3. The only way to produce such a minimum in the calculated linewidths is to assume that the variations in g and A are uncorrelated, in which case (still adding the contributions to the linewidth linearly)

$$\frac{\Delta H}{H} = \left|\left[\left(\frac{x}{S}\frac{\partial S}{\partial x}\right)^{-1} - 1\right]\right|\left(\frac{\Delta A}{A}\right) + \frac{\Delta g}{g} . \tag{10}$$

Then for the best fit, $\Delta g/g = 2\%$ and $\Delta A/A = 3\%$ and the calculated linewidths are as shown in Fig. 3. (If the contributions to the linewidths are squared and then added, the results are much the same.) We have no explanation why the variations in A and g appear to be uncorrelated when they, in fact, are predicted to be directly related as in Eq. (8). This uncorrelated behavior of A and g is an observation which has been made in dielectrics as well.[8]

As was pointed out before, the value of the hyperfine constant A, obtained from these measurements (73.5 G), differs somewhat from the value derived by Tao *et al.*[2] from EPR data at X band (75.0 G). This difference is small but significant in the sense that our value of the hyperfine constant is the same, within experimental error, as that of ^{167}Er in nonmetallic hosts with the same local symmetry as in Au. Tao *et al.*[2] use the difference of the value of A in Au and in dielectric crystals as a measure of the contribution to the hyperfine interaction by the conduction electrons. We have been unable to locate any source of systematic error in our experiment. Furthermore, exactly the same experimental setup, spectrometer, and computer analysis, was used by Szofran[8] in a study of the resonance properties of ^{167}Er in ThO_2 at low temperatures. In that paramagnetic system Szofran found excellent agreement between the value of A deduced from the low-field hyperfine resonances and the results from EPR at X band.[16] If our experimentally observed spectra were fitted with A specified as 75.0 G and only g_n' was kept as an adjustable parameter, the standard deviation in the measured field position from the calculated resonance fields for the six most intense lines is 0.88 G, whereas with the best choice of A of 73.5 G this deviation is only 0.37 G. However, because of the large and uncertain origin of the variation in A required to explain the residual linewidth, perhaps too much should not be made of the difference between the value obtained in this work and that by Tao *et al.*[2]

The width of the resonance line (3, 2), as shown in Fig. 4, exhibits an approximately linear dependence on temperature. Other lines in the spectrum also broadened with increasing temperature consistent with a linear dependence but no careful study has been made of them. If the linewidth is expressed as $\Delta H = a + bT$, the coefficient b is found to be 13 ± 1 G/K for line (3, 2), a temperature dependence five times larger than that observed in the EPR spectra at X band, where $b = 2.5 \pm 0.3$ G/K was obtained in the temperature range $1.5 < T < 6$ K.[3] A linear dependence of the linewidth on temperature is expected when the dominant mechanism for relaxation of the localized paramagnetic ions is through the exchange coupling with the conduction electrons.[17]

The magnitude of the temperature dependence of the linewidth of the direct hyperfine resonance lines differs from that of the EPR line in the microwave region for two reasons. First, the frequency-field relation for the resonances is considerably different such that a broadening $1/T_2 = 2\pi\Delta\nu$ produces a width in field larger by a factor of $(\partial\nu/\partial H)^{-1}_{\text{hyp}}/(\partial\nu/\partial H)^{-1}_{\text{EPR}} \sim 5.8$ for the (3, 2) resonance. Second, the states between which resonance absorption occurs in these measurements are not simply members of an electronic doublet but rather a linear combination of products of electronic and nuclear states, i.e.,

$$|F, m_F\rangle = \alpha\,|M, m\rangle + \beta\,|M-1, m+1\rangle\,, \tag{11}$$

where $|\Gamma', m\rangle \equiv |M\rangle\,|m\rangle$. Exchange of the localized moment with the conduction electrons therefore couples each state to two others within the same multiplet as well as to another pair within the other F multiplet. Since these measurements were carried out at temperatures smaller than the splitting between the two $F = 4$ and $F = 3$ multiplets, $\delta = 4A = 0.14$ K at $H = 0$, the coupling of a state in the lower $F = 4$ multiplet to the states in the upper multiplet should little effect the linewidth of the lower state. The contribution to the linewidth of the coupling of a state to others within the same multiplet will be of the same form as calculated for an electronic doublet except as modified by the degree of admixture as expressed in Eq. (11). Since roughly half of the electronic wave function is associated with the upper $F = 3$ multiplet, the broadening of an individual hyperfine transition would be expected to be in the temperature region below 0.1 K approximately half as great as calculated for an electronic doublet. In making this comparison the splitting of the doublet at X band above 1 K is small compared to kT just as the splitting within the $F = 4$ multiplet is small as compared to kT at 40 mK. From these arguments and the previous measurements at X band, we expect the temperature dependence of the linewidth to be of the magnitude $b \sim 2.5 \times 5.8 \times \frac{1}{2} = 7.3$ G/K, which is smaller than the measured value by a factor of 1.8. The magnitude of this factor is most probably the result of inaccuracies in the experiment as well as not treating the relaxation processes in this multilevel system in sufficient detail.

Finally, we shall comment on the low-temperature-thermometry aspects of the system Au: Er. The relative intensities of the direct hyperfine resonance lines are a direct measure of the temperature of the spin system. Hence, to be able to determine accurately the temperature, the absorption lines have to be numerically integrated with great precision. As we were not able to record the direct absorption spectrum of Au: Er, the large uncertainties inherent in a double integration of the derivative spectrum did not warrant any attempt to make a temperature determination.

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$$\begin{aligned} h\nu = &-g'_n\mu_N H + (\tfrac{1}{2}A)(2I+1)(F-I) \\ &\times [1-2\delta_{m_F+1,p}\,\Theta(x)]\left(1+\frac{4(m_F+1)}{2I+1}x+x^2\right)^{1/2} \\ &-[1-2\delta_{m_F,p}\Theta(x)]\left(1+\frac{4m_F}{2I+1}x+x^2\right)^{1/2} . \end{aligned}$$

Transitions in the two multiplets ($\Delta F=0$, $\Delta m_F=\pm 1$) are degenerate [except for line (4, 3) and for the pseudonuclear Zeeman term $g'_n\mu_N H$, which in the low-field part of the spectrum is very small]. However, the spectrum shown in Fig. 2 was taken at 40–45 mK, at which temperature the population of the higher multiplet ($F=3$) is negligible.

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