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(1979); W. Hanke, in *Festkörperprobleme*, edited by J. Treusch (Vieweg, Wiesbaden, 1979), Vol. XIX, p. 43.

[12]W. Brinkman and B. Goodman, Phys. Rev. 149, 597 (1966).

[13]N. O. Lipari and W. B. Fowler, Phys. Rev. B 2, 3354 (1970).

[14]E. O. Kane, Phys. Rev. B 4, 1910 (1971).

[15]N. E. Brener, Phys. Rev. B 11, 929 (1975).

[16]J. Bennett and J. C. Inkson, J. Phys. C 10, 987 (1977).

[17]S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B 10, 5203, 2602 (1974).

[18]A. B. Kunz, D. J. Mickish, and T. C. Collins, Phys. Rev. Lett. 31, 756 (1973).

[19]J. Hermanson, Phys. Rev. B 6, 2427 (1972).

[20]H. J. Mattausch, G. Strinati, and W. Hanke, to be published.

[21]G. S. Painter, D. E. Ellis, and A. R. Lubinsky, Phys. Rev. B 4, 3610 (1971).

[22]A. Mauger and M. Lanoo, Phys. Rev. B 15, 2324 (1977).

[23]W. Hanke, G. Strinati, and H. J. Mattausch, in Proceedings of the 1980 Annual Conference on Condensed Matter, Antwerp, Belgium (to be published).

NMR Measurement of the Hyperfine Constant of an Excited State of an Impurity Ion in a Solid

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An optically detected NMR measurement of the hyperfine tensor for an excited state of an impurity rare-earth ion (Pr^{3+}) in a solid ($LiYF_4$) is reported. The results have been used to obtain for the first time a measured value of the hyperfine interaction constant $A_j = 616 \pm 51$ MHz of the $^1D_2$ excited state. This is somewhat smaller than the calculated value of 754 MHz.

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We report the first excited-state nuclear magnetic resonance (NMR) observation. From a measurement of the orientation and magnitude of the nuclear Zeeman tensor of the diamagnetic $^1D_2$ (16 740 cm^{-1}) level of trivalent praseodymium dilute in the $LiYF_4$ single crystal, we have obtained the magnetic hyperfine constant[1] A_j for this $^1D_2(4f^2)$ state. Earlier excited-state magnetic-resonance observations were studies of paramagnetic levels.[2-6]

The large nuclear polarization (and population) required for the NMR observation is obtained by high-resolution optical pumping within a strain-broadened inhomogeneous optical line which selects individual hyperfine states. Using this polarization scheme, Erickson[7] has studied the ground-state hyperfine interaction in the trivalent praseodymium in LaF_3 and $YAlO_3$ host crystals. We have extended his optical rf double-resonance technique to an excited state of trivalent praseodymium.

Excited-state studies by Chen, Chiang, and Hartmann[8] have determined the hyperfine splitting of the $^3P_0$ state of Pr^{3+} in LaF_3 from their modulated photon-echo experiments. Erickson,[9,10] using an enhanced and saturated optical-absorption technique, has measured the hyperfine splittings of the lowest level of the $^1D_2$ manifold of states of Pr^{3+} in LaF_3 and $YAlO_3$. The hyperfine constant A_j was not obtained in those studies. Although in principle it should be possible to determine A_j from the hyperfine splittings alone, the lack of the precise knowledge of the pure quadrupole coupling constants and the electronic wave functions make this determination difficult at best. A_j can, however, be determined from knowledge of the nuclear Zeeman tensor without knowing the pure quadrupole constants. The $LiYF_4$:Pr^{3+} system was chosen for study because (i) the $(4f^2)$ electron configuration is the simplest nontrivial rare-earth configuration, (ii) the lowest states of $^1D_2$ and $^3H_4$ are singlets, and (iii) best-fit crystal-field wave functions are available.[11] The low–magnetic-field study of the Pr^{3+} ion in this single-magnetic-site host is greatly simplified compared to the three-magnetic-site LaF_3 host. This magnetic site is axially symmetric, further reducing the complexity (and uncertainty) of the analysis.

We believe a variation of this excited-state NMR technique can be used to obtain the hyperfine and nuclear Zeeman tensors of other systems with nondegenerate electronic states which are inaccessible to the paramagnetic resonance techniques. This knowledge will be useful in the calculation of the optical intensities in the presence of a hyperfine interaction for the interpretation of the modulated photon-echo experiments.[8] It also provides in principle the opportunity to determine the role of the configuration interactions[12] and other interactions such as J-mixing and relativistic corrections in the hyperfine structure in electronic states.

In the $LiYF_4$ crystal,[13] the trivalent praseodymium impurity ion occurs substitutionally for an yttrium ion and has S_4 symmetry.[11] Each electronic multiplet is split into singlets and doublets by the crystal field. As in LaF_3 and $YAlO_3$, the $^3H_4$ and $^1D_2$ manifolds of states both have singlet states lying lowest. Each singlet electronic state is split into three hyperfine doublets by the nuclear electric quadrupole and the second-order magnetic hyperfine interactions. However, the higher rare-earth site symmetry S_4 in $LiYF_4$ requires, in the absence of third- and higher-order hyperfine mixing, that the hyperfine tensor is axial and each hyperfine state may be described as a pure I_z state. Since $\Delta I_z = 0$ optical transitions occur, the optical pumping cycle couples only pairs of levels, which leads to a different type of population distribution from that in the LaF_3 and $YAlO_3$ experiments.

The $^3H_4\,\Gamma_2\,(0\ \mathrm{cm}^{-1})$–$^1D_2\,\Gamma_2\,(16\,740\ \mathrm{cm}^{-1})$ magnetic dipole (zero-phonon) transition of Pr^{3+} (0.05 at.%) in $LiYF_4$ was excited by σ-polarized 2-mm-diam 1-mW focused beam from a single-mode frequency-stabilized laser at 4.5 K. An rf magnetic field of amplitude 0.3 G rms aligned perpendicular to the c axis was slowly frequency swept. The fluorescence from $^1D_2\,\gamma_2$ (16 740 cm^{-1})–$^3H_4\,\Gamma_{3,4}$ (79 cm^{-1}) was monitored. Similar to the Pr^{3+} in LaF_3 and in $YAlO_3$ experiments, fluorescence increases corresponding to ground-state NMR were observed near 9.5 and 19 MHz. These will be discussed elsewhere. However, two decreases in fluorescence were observed at 5123.5 ± 0.9 MHz and $10\,244.6 \pm 0.8$ kHz. One of these is shown in Fig. 1. These results were independent of temperature in the range of 2 to 4.5 K. We believe that these dips represent NMR transitions in the lowest level of $^1D_2$.

A model of the system is shown in Fig. 2. Consider an impurity ion at a site such that the 2-5 transition is resonant with the pump laser. Level 5 relaxes to level 2 primarily through intermediate electronic states. The population of level 5 is a function of the number of pump photons while the sum of the populations of levels 2 and 5 is constant. As for Pr^{3+} in the LaF_3 and $YAlO_3$ host crystals, magnetic dipole transitions between levels 1 or 3, and 2 increase the population of level 2 and therefore increase the optical absorption 2-5 and the monitored fluorescence. On the

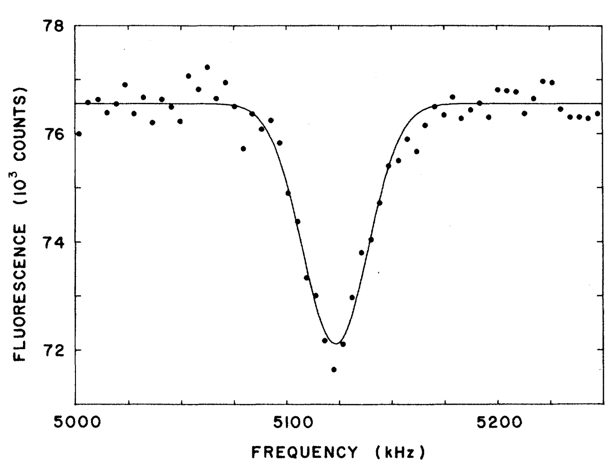

FIG. 1. Optically detected NMR in the lowest $^1D_2$ level of Pr^{3+} in $LiYF_4$. This is the $\frac{1}{2}$-$\frac{3}{2}$ transition. The solid line is a Gaussian curve least-squares best fit to the data. The line is distorted on the high-frequency side because of sweep-rate effects. The resonance frequency is 5123.5 ± 0.9 kHz. The stated error is the standard deviation of the least-squares fit.

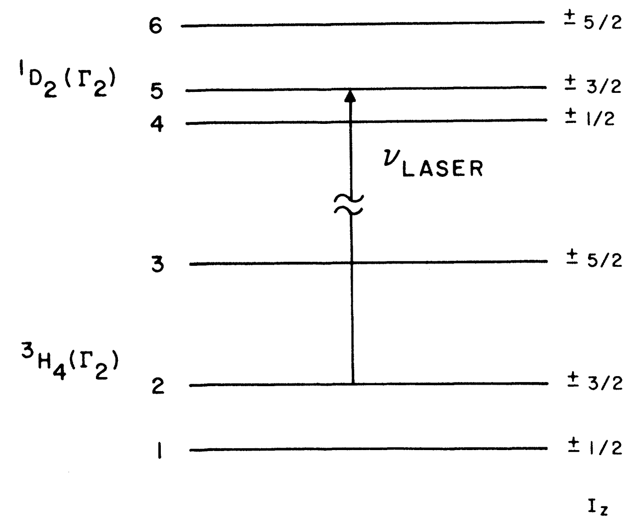

FIG. 2. Energy level model for the optically detected excited-state NMR experiment. Each singlet electronic level is split into three nuclear doublets by the hyperfine interaction. The energy levels are labeled by L, S, J, I_z, Γ_i.

other hand, magnetic dipole transitions between the populated level 5 and the empty levels 4 or 6 remove these ions from resonance with the optical pump (because they relax only to levels 1 and 3, respectively) resulting in a reduction of the optical absorption 2-5 at the laser frequency and a reduction in the monitored fluorescence. A rate equation model confirms these arguments.

Magnetic dipole transitions in any intermediate electronic level would also produce reduction of the fluorescence at resonance. The lifetimes of all levels below the lowest $^1D_2$ level are expected to be much shorter. The relaxation is phonon assisted. The known energy gaps[13] allow four or less phonon processes for all but the lowest $^1G_4$ level. This gives microsecond or less lifetimes for those levels. The lowest $^1G_4$ level must relax through a gap of 2500 cm^{-1} or a five-phonon process in $LiYF_4$. Since the crystal-field splittings are greater for this host than for the LaF_3, the multiphonon rates measured by Riseberg and Moos[14] give an upper bound of 100 μs. This compares to a measured 0.67 ms lifetime for the lowest level of $^1D_2$. Further, the expected value of $\gamma_x = 3.6$ kHz/G for this Γ_1 state ($J_{z(\max)} = 4$), is much larger than the observed value.

The data were fitted to a spin Hamiltonian given by Teplov[15,16]

$$H = \sum_i \gamma_i H_i I_i + D[I_z^2 - \tfrac{1}{3}I(I+1)] + E[I_x^2 - I_y^2],$$
$$i = x, y, z,$$

where

$$D = D_a + P, \quad E = E_a + \tfrac{1}{3}\eta P,$$

with

$$D_a = A_J\left(\frac{\Lambda_{xx} + \Lambda_{yy}}{2} - \Lambda_{zz}\right), \quad E_a = A_J \frac{\Lambda_{yy} - \Lambda_{xx}}{2};$$

D_a, E_a represent the second-order magnetic-hyperfine-interaction contributions and P, η are the pure quadrupole parameters;

$$\gamma_i = (-g_N\mu_N - 2g\mu_B\Lambda_{ii})/h$$
$$\Lambda_{ii} = \sum_{n\neq 0} A_J \frac{|\langle 0|J_i|n\rangle|^2}{\epsilon_n - \epsilon_0};$$

ϵ_n = energy of level n and A_J = hyperfine constant appropriate to the electronic state studied.[1] The results are $D = +2561 \pm 0.6$ kHz, $|E| = 17 \pm 8$ kHz, $\gamma_z = -1.653 \pm 0.020$ kHz/G, $\gamma_x = \gamma_y = -1.480 \pm 0.020$ kHz/G. The magnetic splitting parameters were derived from a simultaneous least-squares fit of the Hamiltonian to 37 frequencies measured at fields of 30 ± 0.1 G, 40 ± 0.1 G at many different angles between the field vector and the crystal c axis. The z axis of the hf tensor is found to be parallel to the crystallographic c axis within a degree. The rf frequency for each channel was measured to an accuracy of 0.2 kHz. The stated errors of D, E, and γ are the standard deviations obtained from the least-squares analysis.

The hyperfine constant A_J was determined by use of $\gamma_i = -(g_N\mu_N + 2g\mu_B\Lambda_{ii})/h$, the measured values of γ_x, γ_z, and the crystal-field intermediate-coupling wave functions of Esterowitz[11]: From γ_z, $A_J = +609 \pm 40$ MHz, and from γ_x, $A_J = +630 \pm 74$ MHz. The value of $A_J(^1D_2) = +754$ MHz calculated from the formulas of Wybourne[1] (with corrections for intermediate couplings) and the experimental ground-state value from Teplov [15] is significantly higher. The reliability of the "measured" A_J is dependent on the accuracy of the crystal-field wave functions and of the intermediate-coupling corrections. The intermediate coupling states are well known for praseodymium. The intermediate-coupling corrections represent a 10% effect, and if they are known to 10%, give a 1% accuracy for the calculated A_J. The crystal-field states in D_{2d} symmetry with $J = 2$ are completely symmetry determined except for the intermediate-coupling coefficients. Since Esterowitz[11] has demonstrated that the praseodymium site symmetry is only slightly distorted from D_{2d}, the uncertainty in the "measured" A_J from incomplete knowledge of the crystal-field wave functions is small indeed. Interactions such as the configuration interaction and J mixing which have been ignored in the analysis may make a significant contribution to the discrepancy.[12] However, knowledge of the A_J's for several excited states would be required before an experimental estimate can be made of their contributions.

The measured D_g and D_e for the ground $^3H_4$ (0 cm^{-1}) and excited $^1D_2$ (16 740 cm^{-1}) states together with the calculated second-order magnetic hyperfine contribution D_a(excited) = -0.039 MHz and D_a(ground) = $+3.262$ MHz were used to determine the pure quadrupole parameters[17] $P_{\rm lat}$ and P_{4f} for the ground and excited states [$P_{4f}(^3H_4) = 0.76$ MHz, $P_{4f}(^1D_2) = 1.88$ MHz, and $P_{\rm lat} = 0.71$ MHz]. The asymmetry parameter η was assumed to be zero. The calculated ratio of $P_{4f}(^1D_2)/P_{4f}(^3H_4) = 2.47$ was used in this fit. $P_{\rm lat}$ was assumed to be the same in the two electronic states as the total $4f$ electron shielding of the nuclear quadrupole moment from the lattice is less than 3%.[18] Shielding changes from one electronic state to another should represent a small fraction of that.

If the impurity ion exists in a site of lower than axial symmetry, certain modifications in the experimental technique are required to observe excited-state NMR. It can be shown in the steady state that optical pumping in the absence of ground-state magnetic dipole transitions completely depopulates the pumped level (level 2). Since the population of level 5 is always less than that of level 2 at the pump levels used in these experiments, no NMR can be observed in the excited state. However, we believe excited-state NMR of Pr^{3+} may be observed in LaF_3 and $YAlO_3$ if the crystal is simultaneously radiated at one or both of the ground-state frequencies in addition to the excited-state frequency.

In conclusion, this experiment demonstrates the feasibility of study of the excited-state hyperfine interaction of impurities in solids through optically detected NMR measurements. The results will be useful in the calculation of optical intensities in the presence of the hyperfine interaction. This technique will broaden the study of the configuration interactions through the use of the knowledge gained by excited-state NMR experiments. This hyperfine knowledge might also serve to supplement the crystal-field data in lower-symmetry situations, particularly for Pr^{3+} in LaF_3, in order to obtain a unique symmetry, and crystal-field eigenfunctions where the number of parameters is too large to obtain a satisfactory fit from the crystal-field energy levels alone.

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[a]On leave from the Indian Institute of Technology, Kanpur, India.

[1]B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965), p. 115.

[2]B. Cognac, J. Brossel, and A. Kastler, C. R. Acad. Sci. 246, 1827 (1958). This paper concerns the optical detection of NMR in diamagnetic ground state.

[3]J. Brossel and F. Bitter, Phys. Rev. 86, 308 (1952).

[4]W. J. Childs, O. Poulsen, and L. S. Goodman, Phys. Rev. A 19, 160 (1979).

[5]Dietmar Stehlik, in *Excited States*, edited by Edward C. Lim (Academic, New York, 1977), Vol. 3; K. P. Dinse and C. T. Winscom, Semicond. Insulat. 4, 263 (1978).

[6]S. Geschwind, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972); J. P. Hessler and C. A. Hutchison, Jr., Phys. Rev. B 8, 1822 (1973).

[7]L. E. Erickson, Opt. Commun. 21, 147 (1977).

[8]Y. C. Chen, K. Chiang, and S. R. Hartmann, Opt. Commun. 29, 181 (1979).

[9]L. E. Erickson, Phys. Rev. B 16, 4731 (1977).

[10]L. E. Erickson, Phys. Rev. B 19, 4412 (1979).

[11]L. Esterowitz, F. J. Bartoli, R. E. Allen, D. E. Wortman, C. A. Morrison, and R. P. Leavitt, Phys. Rev. B 19, 6442 (1979); L. Esterowitz, F. J. Bartoli, and R. E. Allen, J. Lumines. 21, 1 (1979).

[12]B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965), p. 151.

[13]R. E. Thoma, C. F. Weaver, H. A. Friedman, H. Insley, L. A. Harris, and H. A. Yakel, Jr., J. Phys. Chem. 65, 1096 (1961).

[14]L. A. Riseberg and H. W. Moos, Phys. Rev. 174, 429 (1968).

[15]M. A. Teplov, Zh. Eksp. Teor. Fiz. 53, 1510 (1967) [Sov. Phys. JETP 26, 872 (1968)].

[16]The sign of $g_n\beta_n$ terms in Teplov's Eq. (2) should be negative. See B. Bleaney, in *Proceedings of the Third International Conference on Quantum Electronics, Paris, 1963*, edited by P. Grivet and N. Bloembergen (Columbia Univ. Press, New York, 1964), p. 607.

[17]S. Hüfner, *Optical Spectra of Transparent Rare Earth Compounds* (Academic, New York, 1978); B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963), p. 91.

[18]K. D. Sen and P. T. Narasimhan, Phys. Rev. B 16, 107 (1977).