

Nuclear Double Irradiation in Sodium Bromate*

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Two different frequency magnetic resonance transitions involving a common energy level are observed simultaneously using the Br^{79} nuclear quadrupole energy levels split by a magnetic field of 7000 G. Irradiation of different transitions with frequencies near 180 Mc/sec may enhance the absorption of a transition near 14 Mc/sec, or produce population inversion enabling observation of a stimulated emission at the lower frequency. The dependence of the enhancement on the rf voltage of the 180-Mc/sec oscillator is shown.

WE have produced an increase in the intensity of a 13.6-Mc/sec nuclear magnetic resonance absorption between two energy levels by maintaining a reduced population of the upper level with a nuclear spin transition at 176 Mc/sec. All of our observations have been at room temperature. Only one nuclear species Br^{79} is involved. These nuclei are in a single crystal of NaBrO_3 of volume about one-half cubic inch. In the absence of a magnetic field, a pure nuclear quadrupole transition at about 179 Mc/sec is observed.¹ The energy levels for these nuclei in a magnetic field of 6657 G, and for an angle θ of 70° between the crystalline electric field gradient symmetry axis and the magnetic field direction, are shown in Fig. 1.² The states associated with the two lowest energy levels are combinations of pure $m = +\frac{1}{2}$ and $m = -\frac{1}{2}$ states, so that four transitions with frequencies near 179 Mc/sec are observable, as well as the 13.6-Mc/sec transition between these levels.

Two rf oscillators were used to excite resonances ν_{42} and ν_{21} simultaneously. The crystal was carefully oriented so that two of the field gradient axes were within less than 0.1° of the same angle, about 70° , from the magnetic field direction. A typical chart record is shown in Fig. 2. The magnetic field is not varied except for a 1-G peak-to-peak 33-cps modulation. From point A on the chart the frequency of the low-frequency (~ 13 Mc/sec) oscillator is increased while the chart records the derivative of the ν_{21} absorption, obtained with the usual narrow band techniques. At B the low-frequency drive is stopped when one of the derivative maxima is reached, and the chart pen is manually shifted to B'. The frequency of the high-frequency (~ 176 Mc/sec) oscillator has been set away from any resonance, and now from B' to C it is varied through the ν_{42} absorption, producing an increase of the ν_{21} derivative maximum. From C to C' the pen is manually shifted, and from C' the low-frequency drive is resumed to complete the unenhanced derivative.

We take $(a+b)/a$ from the chart record as a measure

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¹ T. P. Das and E. L. Hahn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Suppl. I.

² Y. Ting, E. R. Manring, and D. Williams, *Phys. Rev.* **96**, 408 (1954).

of the absorption enhancement. A relative measure of the rf voltage level of the 176-Mc/sec oscillator is obtained with a pickup coil, diode, and microammeter. The dependence of the enhancement on this rf level is shown in Fig. 3. We were unable to obtain data with higher rf voltages because of too great frequency instability of the high-frequency oscillator. We followed the above procedure, stopping the low-frequency oscillator on both the positive and negative derivative maxima of the ν_{21} transition. We found that the frequency of the high-frequency oscillator for maximum enhancement of the positive derivative was always 1–5 kc/sec lower than when enhancing the negative derivative. This frequency difference is about the same as the width of the ν_{42} absorption,³ and is consistent with a more detailed energy level diagram which includes level broadening by nuclear dipole-dipole interactions.

The values of ν_{42} given in Fig. 3 are for the limit of vanishing high-frequency voltage. Because of heating of the high-frequency rf coil, the temperature of the NaBrO_3 crystal increased by as much as 4°C with the highest voltage levels. This reduced the quadrupole

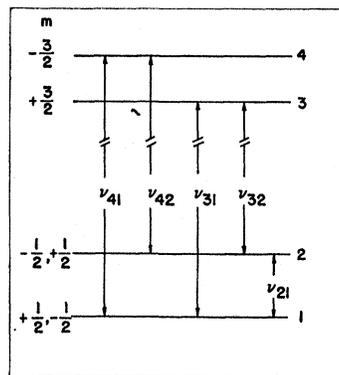


FIG. 1. Energy levels and magnetic resonance transitions of Br^{79} nuclei in NaBrO_3 for a magnetic field of 6657 G and an angle θ of 70° between the crystalline electric field gradient symmetry axis and the magnetic field direction. The two lowest energy states are combinations of $m = \pm\frac{1}{2}$ states. $\nu_{31} = 182.5$ Mc/sec, $\nu_{42} = 175.9$ Mc/sec, and $\nu_{21} = 13.6$ Mc/sec.

³ Y. Koi, *J. Phys. Soc. Japan* **12**, 49 (1957).

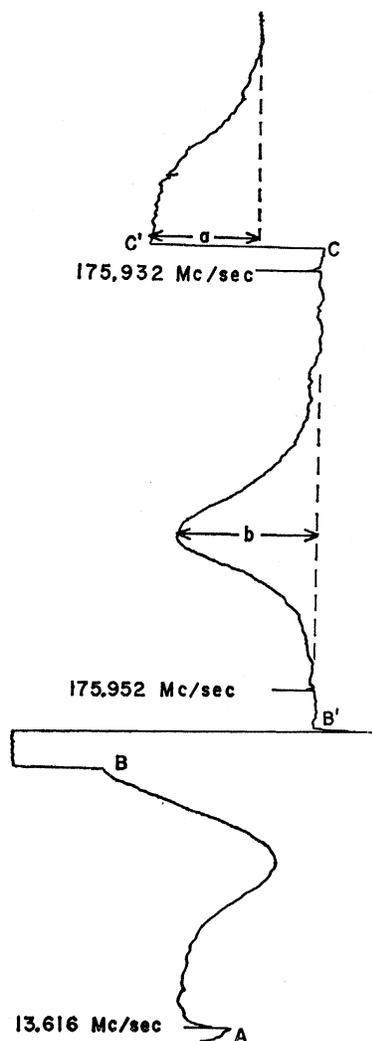


FIG. 2. Chart record showing enhancement of the derivative maximum of absorption ν_{21} . The unenhanced derivative maximum is a ; the increase of the derivative maximum due to irradiation of absorption ν_{42} occurs between B' and C . The greatest enhancement is $(a+b)/a$. For the particular record shown $(a+b)/a = 2.3$, and at maximum enhancement, $\nu_{42} = 175.945$ Mc/sec. This is lower than the value of ν_{42} given in Fig. 3 as explained in the text.

interaction, so the actual values of ν_{42} for maximum enhancement were up to 50 kc/sec lower than the value given in Fig. 3. The values of ν_{21} were insignificantly changed by this temperature rise.

When the procedure to obtain the record of Fig. 2 was followed, but with the high frequency varied through ν_{31} instead of ν_{42} , the intensity of the ν_{21} absorption was decreased, and with sufficient high-frequency rf voltage, the chart pen was driven to the opposite side of the chart base line. This indicates stimulated emission at 13.6 Mc/sec, and is similar to the observations of Kushida and Silver.⁴

The above observations can be understood in terms of changes of the difference of the nuclear spin populations of the two lowest energy levels, since the absorption intensity is proportional to $n_1 - n_2$. Solving simultaneous rate equations for the level populations, for the case of saturation of the ν_{42} resonance ($A_{24} \gg P_{ij}$'s, A_{12}),

we obtain

$$n_1 - n_2 = \frac{Nh}{4kT} \left[\frac{2P_{12}\nu_{21} + 2P_{14}\nu_{41} + P_{13}\nu_{31} - P_{23}\nu_{32}}{2P_{12} + 2P_{13} + 2P_{14} + 2A_{12} - P_{23}} \right]. \quad (1)$$

The P_{ij} 's are combinations of the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ quadrupolar and $\Delta m = \pm 1$ magnetic relaxation transition probabilities. The A_{ij} 's are induced transition probabilities. Since for $\theta = 70^\circ$ the two lowest energy states are mixtures in about equal parts of the $m = \pm \frac{1}{2}$ pure states, we approximate with $P_{14} \approx P_{13} \approx P_{24} \approx P_{23} \gg P_{12}$. We find an increase of $n_1 - n_2$ given by Eq. (1), compared with the case for $A_{24} = 0$, of a factor of approximately $2\nu_{41}/3\nu_{21}$. This is about 9 for $\nu_{21} = 13.6$ Mc/sec and $\nu_{41} = 190$ Mc/sec. When ν_{21} was reduced to 7.12 Mc/sec while ν_{42} and ν_{41} changed by less than 3%, greater enhancements were obtained, as shown in Fig. 3. Emission is predicted when the rate equations are solved for the case of saturation of the ν_{31} resonance.

Stimulated emission at 7.12 Mc/sec was also observed for the case of the field gradient axis oriented at 0° from the magnetic field direction. For this angle the lowest energy states are pure states, and P_{14} and P_{23} are not, in general, equal to P_{13} and P_{24} .⁵ The intensity of the emission for $\theta = 0^\circ$ was observed to be a factor of 2 or 3 greater than for $\theta = 70^\circ$, for the same high-frequency rf levels.

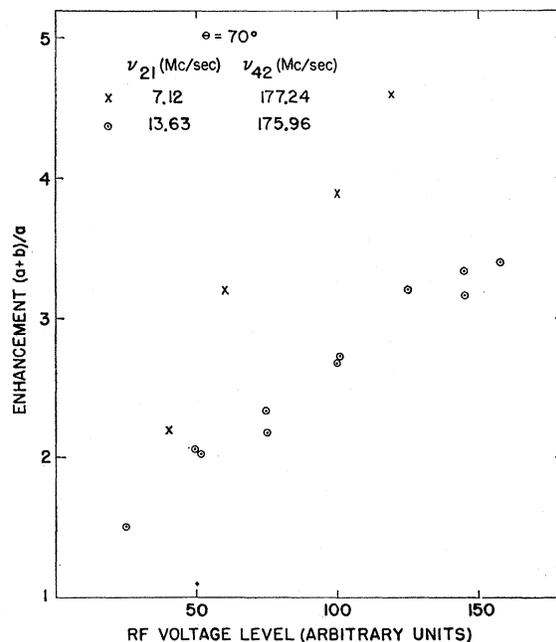


FIG. 3. Measured enhancements of the ν_{21} derivative maximum for different rf voltage levels of the ~ 176 -Mc/sec oscillator whose frequency is swept through the absorption at ν_{42} . The values of ν_{42} are for the limit of low voltage. The uncertainty of the enhancement values is ± 0.2 for the 13.6-Mc/sec data and ± 0.5 for the 7.1-Mc/sec data.

⁴ T. Kushida and A. H. Silver, Phys. Rev. **130**, 1692 (1963).

⁵ M. J. Weber, Phys. Chem. Solids **17**, 267 (1961).

An unusual observation was made when the high frequency was set within the ν_{31} absorption width, and the low frequency was driven through the ν_{21} resonance without stopping on a derivative maximum. With this procedure the low-frequency side of the ν_{21} resonance exhibited absorption, while emission occurred on the high-frequency side.

The object of further work will be to get information

about the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ relaxation probabilities, using pulse techniques as well as steady-state resonance.^{5,6} Because the nuclear magnetic quality factor is orders of magnitude larger than the Q for a circuit operating at a few Mc/sec, we do not expect maser operation with this spin system.⁷

⁶ W. I. Goldberg, Bull. Am. Phys. Soc. 4, 251 (1959).

⁷ J. Itoh, J. Phys. Soc. Japan 12, 1053 (1957).

Calculation of the g Factor of Hydrogen and the Alkali Atoms Trapped in Rare-Gas Solids

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The author's variational method of calculating g -factor shifts for atomic hydrogen trapped in a rare-gas solid is applied to the case of the alkali metals as impurities. An alternate derivation of the results is given and a simple physical model is discussed. The calculated shifts are compared with the experimentally observed ones for H, Li, Na, and K trapped in Ne, Ar, and Kr. Reasonable agreement is obtained if it is assumed that where two resonances have been reported the impurities are trapped at substitutional and octahedral interstitial lattice sites. The connection between the variational formalism and a previous perturbation treatment of Adrian is discussed and it is shown that a reinterpretation of the latter yields improved agreement with experiment. Crude estimates of the relaxation about substitutional and interstitial impurities are also given.

INTRODUCTION

THE experiments of Jen *et al.*^{1,2} on the spin resonance of atomic hydrogen trapped in rare-gas solids at low temperature have led to the development of several explanations of the observed departure from free atomic hydrogen electron spin resonance spectra.^{3,4} Recently, additional experimental results have become available for the paramagnetic resonance of the alkali metals trapped in rare-gas solids.^{5,6} These provide a test of the theories and comparison with theory suggests what trapping sites are occupied in the experiments.

In this paper the author's variational method of calculating the g -factor shift is rederived for the alkali rare-gas systems by using Schmidt-orthonormalized

wave functions to avoid the problems of convergence of the Löwdin overlap series.⁴ Several physical models for picturing the mechanism by which the shifts occur are discussed in detail to supplement the formal development of Ref. 4. In addition, a comparison of the predictions of the variational calculation and perturbation theory calculations is made from several points of view.

Numerical values of the g -factor shifts are given for the variational calculation, the perturbation theory approach due to Adrian³ and a modification of the perturbation formalism. It is found that the variational approach and the modified perturbation theory give reasonable agreement with experiment for the cases in which the impurity atom may be reasonably assigned to simple substitutional or interstitial sites.

THEORY

The problem of an impurity center in a rare-gas solid other than helium may be approached most reasonably from a static-lattice, tight-binding approximation. A zeroth-order approximation to the one-electron wave functions for such a system is given by the Hartree-Fock atomic functions. These, however, must be modified to take into account the spin-orbit, crystal field, and van der Waals interactions as well as wave function overlap in the crystal.

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¹ C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 104, 846 (1956).

² S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. 32, 963 (1960).

³ F. Adrian, J. Chem. Phys. 32, 972 (1960).

⁴ D. Y. Smith, Phys. Rev. 131, 2056 (1963).

⁵ C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, Phys. Rev. 126, 1749 (1962).

⁶ J. P. Goldsborough and T. R. Koehler, Bull. Am. Phys. Soc. 7, 449 (1962).