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<sup>1</sup>R. S. Mulliken, in The Threshold of Space, edited by M. Zelikoff (Pergamon Press, New York, 1957).

<sup>2</sup>H. Lefebvre-Brion and C. M. Moser, *J. Chem. Phys.* **43**, 1394 (1965).

<sup>3</sup>H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, *J. Chem. Phys.* **44**, 355 (1966).

<sup>4</sup>E. N. Lassetre, A. Skerbele, and V. D. Meyer, **45**, 3214 (1966).

<sup>5</sup>G. E. Chamberlain, H. G. M. Heideman, J. A. Simpson, and C. E. Kuyatt, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada, 1965 (W. A. Benjamin Inc., New York, 1965).

<sup>6</sup>R. E. Worley, *Phys. Rev.* **64**, 207 (1943).

<sup>7</sup>This identification of the "i" bands has been proposed recently by one of us [K. Dressler, in Proceedings of the International Conference on Spectroscopy,

Bombay, India, 1967 (to be published)], and we are greatly indebted to Professor Worley for sending us a print of his spectrogram to help clarify this question. Our own spectrograms at higher pressures clearly verify the proposed assignment, and Dr. P. K. Carroll (private communication) has independently made the same assignment on the basis of detailed rotational analyses.

<sup>8</sup>Dressler, Ref. 7.

<sup>9</sup>This estimate is based on the  $f$  values of the  $v''=0$  progression given in G. M. Lawrence, D. L. Mickey, and K. Dressler (to be published) combined with approximate Franck-Condon factors  $q(1-0)$  and  $q(1-1)$  adopted from R. W. Nicholls, *J. Quant. Spectr. Radiative Transfer* **2**, 433 (1962).

<sup>10</sup>Lawrence, Mickey, and Dressler, Ref. 9.

<sup>11</sup>Y. Tanaka, private communication.

### SOME NEW SCHEMES FOR POLARIZING NUCLEI\*

C. D. Jeffries

Department of Physics, University of California, Berkeley, California  
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Although nuclei in gases have been polarized using the method of optical pumping introduced by Kastler,<sup>1</sup> no successful experiments have yet been reported for solids. In this note we give details on some new schemes recently proposed<sup>2</sup> for enhancement of nuclear polarization by optical pumping in solids, abbreviated as ENPOPS. Although there are several cases discussed below, the schemes have these general features: (1) production of an electron spin polarization by pumping with circularly polarized light; (2) transfer of this polarization to nuclear spins through hfs coupling, preferential relaxation processes, or saturation of microwave transitions; (3) transfer of the polarization to abundant nuclei through cross relaxation. In principle, ENPOPS could produce sizable nuclear polarization even at room temperatures, which is an advantage over the present microwave dynamic nuclear polarization methods.<sup>3</sup>

(A) Contact hfs, high fields.—To consider this case imagine a magnetically dilute crystal at a temperature  $T$  containing paramagnetic ions, or perhaps  $F$  centers or trapped atoms, in which the electronic ground state is represented by the spin Hamiltonian  $\mathcal{H} = g\beta\vec{H} \cdot \vec{J} + A\vec{J} \cdot \vec{I}$ , the large first term representing the Zeeman interaction of the ion with an external magnetic field  $H$  and the second, the hfs interaction with the nucleus of the ion (or in the case of

$F$  centers, with a near-neighbor nucleus). These energy levels and wave functions ( $J, J_z, I_z$ ) are shown in Fig. 1 for  $J = \frac{1}{2}$  and  $I = \frac{1}{2}$ , along with an optical level or band to which we induce transitions by illuminating the crystal with circularly polarized light. We assume that by pumping with, say, right-hand polarized light we induce the transition probabilities shown,

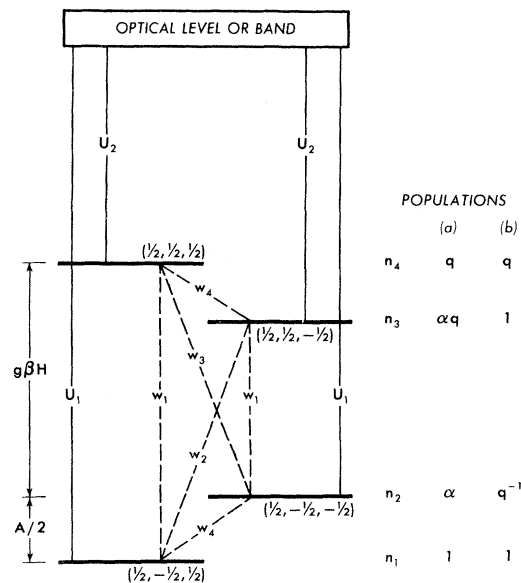


FIG. 1. Levels and transitions for a paramagnetic ion in high field with  $S = \frac{1}{2}$  and  $I = \frac{1}{2}$ . The populations in columns (a) and (b) are obtained by enhancement of the nuclear polarization by optical pumping.

where  $U_2$  is significantly different from  $U_1$ . This comes about because the field decouples the electron and the nucleus, and the light wave is coupled only to the electron; the transitions obey the selection rule  $\Delta J_z = +1$ ,  $\Delta I_z = 0$ . For example, if the ground state is  ${}^2S_{1/2}$  and the excited state is  ${}^2P_{1/2}$ , the relative transition probabilities are<sup>4</sup>  $U_1 = 2$  and  $U_2 = 0$ ; if the excited state is  ${}^2P_{3/2}$ , then  $U_1 = 1$  and  $U_2 = 3$ . If we pump both states of the  $LS$  multiplet, however, then  $U_1 = U_2$ ; in solids where the optical lines or bands may be broad we thus require a sufficiently large spin-orbit coupling to partially resolve the multiplets in order to selectively pump out of the ground state. To quote examples of feasibility, Faraday rotation and magnetic circular dichroism measurements show that one can obtain  $U_2/U_1 \approx 3$  by pumping the  $4f-5d$  bands in rare-earth ions<sup>5</sup>; and  $U_2/U_1 \approx 1.1$  to 2 in  $F$  centers in alkali halides.<sup>6</sup>

In Fig. 1,  $w_1$  represents the paramagnetic spin-lattice relaxation arising from the thermal modulation of the crystalline electric fields;  $w_2$  and  $w_3$  represent relaxation arising, say, from modulation of the hfs interaction  $A'(t)(J_+I_- + J_-I_+)$ , which makes  $w_2 \gg w_3$ . It is just this preferential relaxation which makes the Overhauser effect possible.<sup>7,8</sup> In considering the downward relaxation from the optical level we postulate two extreme cases.

(1) Nuclear spin memory. This means that ions optically pumped out of the left-hand side of Fig. 1 ( $I_z = +\frac{1}{2}$ ) will decay to the left-hand side before thermalization can occur; and ions on the right-hand side return to the right. The over-all effect of pumping with circularly polarized light in competition with  $w_1$  is to establish the relative populations shown in column (a), where  $q = U_1/U_2$  for strong pumping and  $\alpha$  is to be determined by the relaxations  $w_2$  and  $w_3$ . For  $w_2 \gg w_3$  thermal equilibrium requires  $\alpha q = \exp(-g\beta H/kT) \equiv \exp(-\Delta)$ . This ideal ENPOPS thus yields a nuclear polarization

$$p = \frac{n_1 + n_4 - n_2 - n_3}{n_1 + n_4 + n_2 + n_3} = \frac{q - \exp(-\Delta)}{q + \exp(-\Delta)}. \quad (1)$$

We assume that the population of the optical level remains negligible. Solution of the rate equations for arbitrary light intensity yields

$$p = \frac{(U_1/w_1) - (U_2/w_1) \exp(-\Delta)}{4 \exp(-\frac{1}{2}\Delta) + (U_1/w_1) + (U_2/w_1) \exp(-\Delta)}. \quad (2)$$

Half-saturation occurs for  $U \sim T_1 e^{-1} \exp(-\frac{1}{2}\Delta)$ , where  $T_1 e^{-1}$  is the ground-state relaxation

rate. At very low temperatures, where  $q \gg \exp(-\Delta)$ , Eq. (1) shows that the nuclear polarization is essentially complete and obtains even if  $q = 1$ , i.e., for unpolarized light and even if  $U_1 = U_2$ . At high temperatures,  $\exp(-\Delta) \approx 1$ , and Eq. (1) becomes

$$p = (q-1)/(q+1), \quad (3)$$

showing that a large polarization could be obtained even at room temperatures. Reversing the light polarization requires that  $q \rightarrow 1/q$ , which reverses the sign of  $p$ . For an oscillator strength of order unity and moderate pumping intensities ( $\sim W/cm^2$ ) it is possible to achieve  $U \sim 10^6 \text{ sec}^{-1}$ , which is comparable with  $T_1 e^{-1}$  for favorable substances at room temperature. If we cannot be sure that  $w_2 \gg w_3$ , then one knows from dynamic nuclear polarization<sup>9</sup> that it is feasible to saturate the forbidden microwave transition  $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) \leftrightarrow (\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ . This together with optical pumping will lead to the populations of column (b), and a polarization given by Eq. (3), again large and independent of temperature. This is essentially because in ENPOPS the enhanced polarization is determined by matrix element ratios rather than by Boltzmann factors as in dynamic polarization.

(2) Randomized optical relaxation. In this case we postulate that ions in the optical band relax with equal probability to the four ground levels. Solution of the rate equations shows that very strong optical pumping yields no nuclear polarization, because the optical relaxation in effect short circuits the relaxations  $w_2$  and  $w_3$ ; however, at intermediate light intensities a polarization is obtained if  $w_1 \approx w_2 \gg w_3$ , a requirement met in  $F$  centers, for example. Or instead one could saturate the forbidden microwave transition yielding again the polarization of Eq. (3).

It is possible to transfer the polarization of the rather few nuclei of the ions to the abundant nuclei  $I'$  at diamagnetic sites in the crystal by cross relaxation, for example, by operating in a field such that  $g_n' \beta H = \frac{1}{2}A$ ; it is well known that the polarization will diffuse throughout the sample by rapid mutual spin flips. Alternatively, one could pulse on the field to this value simultaneously with an intense light pulse, thus making an optically pumped nuclear-spin refrigerator.<sup>10</sup>

(B) Contact hfs, low fields.—Consider the same system but with the hfs term much larger than the Zeeman, with the levels as in Fig. 2.

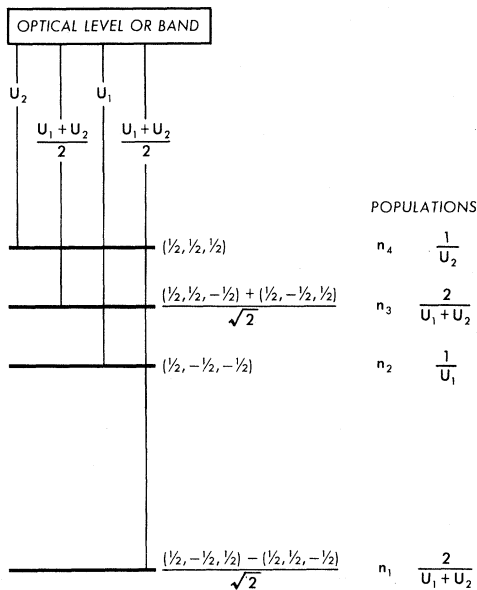


FIG. 2. Levels and transitions for a paramagnetic ion in very low field with  $S = \frac{1}{2}$  and  $I = \frac{1}{2}$ . The populations are obtained by ENPOPS.

The admixing by the hfs puts an optical handle on the nuclear spins, with the transition probabilities shown. If the crystal is strongly pumped with, say, right-hand circularly polarized light, the populations shown will obtain for randomized optical relaxation and with no restriction on the relative magnitudes of spin-lattice relaxation rates within the ground state. This method of ENPOPS yields a nuclear polarization

$$p = \frac{n_4 - n_2}{n_1 + n_2 + n_3 + n_4} = \frac{U_2^{-1} - U_1^{-1}}{4(U_1 + U_2)^{-1} + U_2^{-1} + U_1^{-1}} \quad (4)$$

This is a sizable effect, temperature independent, and reversible by using left-hand polarized light. Equation (4) is valid for  $H \approx 0$ ; for  $g\beta H \sim A$ , the polarization is somewhat larger. It should be possible to transfer this polarization to the abundant nuclei  $I'$  by a three-spin cross-relaxation process in low field between two ions and a neighbor nucleus, or by isentropic pulsing to high fields, where  $g'\beta H = \frac{1}{2}A$ .

(C) Dipolar coupling. — For a paramagnetic ion or atom in dipole-dipole coupling with the nucleus of a neighboring diamagnetic atom, the high-field levels will be similar to those of Fig. 1. Since  $w_2 = w_3$  for dipolar coupling in solids,<sup>8</sup> it will not generally be possible to achieve a polarization by optical pumping alone. However, by also saturating the forbidden mi-

crowave transition  $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) \leftrightarrow (\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ , the populations of Fig. 1 column (b) result, with a polarization given by Eq. (3). The possible advantage this variety of ENPOPS may have over straight microwave dynamic polarization is that, in principle, it will give large nuclear polarizations at room temperature, which could be very rapidly reversed by reversal of the light polarization.

(D) Diamagnetic solids. — To fix ideas, consider a crystal containing ions or atoms with a  $^1S_0$  ground state and a  $^3P_1$  optically excited state, in hfs interaction with a nucleus of spin  $I = \frac{1}{2}$ . In low fields the levels are as in Fig. 3, characterized by  $M_F$ . Also shown are the relative transition probabilities for polarized light. In a spin refrigerator mode of operation one could preferentially populate the hfs levels of the excited state by a pulse of right circularly polarized light ( $\sigma^+$ ); this polarization could be transferred by cross relaxation to abundant nuclei in the ground state, which have a very long relaxation time when the light is off. Another mode of operation is possible if the optical de-excitation is by prompt spontaneous emission before thermalization which repopulates the  $M_F = +\frac{1}{2}$  ground state at  $\frac{5}{3}$  the rate of repopulation of the  $M_F = -\frac{1}{2}$  state. The hfs relaxation  $w_5$  will further contribute to the buildup of the ground-state nuclear polarization, as will induced microwave transitions. If the return relaxation is completely randomized, however, there will be no polarization induced since there is no preferential pumping from the ground state, assuming that the hfs is not resolved in solids.

Recently, a small polarization of the protons

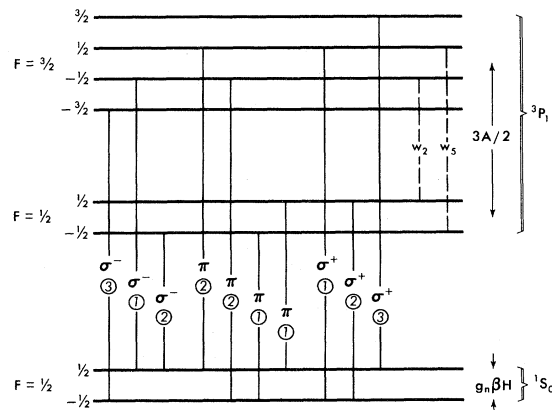


FIG. 3. Levels and optical transitions for a substance with a  $^1S_0$  ground state and a  $^3P_1$  excited state.

in anthracene has been reported, through pumping with unpolarized light<sup>11</sup>; this comes about because of selective de-excitation of higher bands to the magnetic states of an excited triplet, and is a different mechanism from that considered here.

(E) Liquids.—The basic ideas of the above ENPOPS schemes can be readily extended to liquids containing paramagnetic ions or other magnetic species, provided that  $U_1$  and  $U_2$  can be made sufficiently different (this usually requires large spin-orbit coupling), and that the oscillator strength and available light intensity combine to give  $U \sim T_1 e^{-1}$ , required for optical saturation. The nuclei of interest are those in the abundant diamagnetic solvent molecules, which have a rapidly fluctuating interaction with the ion, either of the hfs form  $\vec{I} \cdot \vec{A} \cdot \vec{S}$  or of dipole-dipole form. The first case is similar to (A) above except that the hfs is averaged out. However,  $w_2 \gg w_3$  if the hfs fluctuation is nearly isotropic, and we conclude that if nuclear-spin memory exists, then pumping the liquid with circularly polarized light will yield the nuclear polarization of Eq. (3). For the dipolar case in liquids<sup>8</sup>  $w_2:w_3:w_4 = 2:12:3$  and one should find a reversed nuclear polarization.

It can also be shown that ENPOPS should

apply to magnetically concentrated substances which display an Overhauser effect.

Experiments to test these various cases are underway at the University of California, Berkeley, California. It is a pleasure to acknowledge a stimulating discussion with Professor P. L. Scott, leading to Case (B) above.

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<sup>1</sup>A. Kastler, *J. Phys. Radium* **11**, 255 (1950).

<sup>2</sup>C. D. Jeffries, invited paper at the International Conference on Hyperfine Interactions by Detection of Nuclear Radiation, 28 August 1967 (to be published).

<sup>3</sup>See, e.g., C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience Publishers, Inc., New York, 1963).

<sup>4</sup>See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed. p. 292.

<sup>5</sup>C. H. Anderson, H. A. Weakliem, and E. S. Sabisky, *Phys. Rev.* **143**, 223 (1966).

<sup>6</sup>N. V. Karlov, J. Margerie, and V. Merle D'Aubigne, *J. Phys. Radium* **24**, 717 (1963).

<sup>7</sup>A. Overhauser, *Phys. Rev.* **89**, 689 (1953).

<sup>8</sup>A. Abragam, *Phys. Rev.* **98**, 1729 (1955).

<sup>9</sup>C. D. Jeffries, *Phys. Rev.* **106**, 164 (1957), and **117**, 1056 (1960).

<sup>10</sup>C. D. Jeffries, *Cryogen.* **3**, 41 (1963); A. Abragam, *Cryogen.* **3**, 42 (1963).

<sup>11</sup>G. Maier, U. Haeblerlen, H. C. Wolf, and K. H. Hausser, *Phys. Letters* **25A**, 384 (1967).

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### THICKNESS OF A ROTATING LIQUID-HELIUM FILM\*

R. E. Little† and K. R. Atkins

Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania

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The thickness of a rotating liquid-helium film has been measured at various angular velocities and temperatures. The results are consistent with hydrodynamical calculations assuming that the superfluid component remains at rest and that the normal component alone rotates. The failure to induce rotation in the superfluid component is interpreted as evidence that vortex lines with their axes perpendicular to the film are difficult to create.

Rotation experiments fall into several classes. If a bulk sample of helium is used, the critical velocity is very small and its effects are difficult to observe. Experiments in which flow takes place in packed powders or their equivalent obtain large critical velocities but have complex geometries. In such experiments rotation probably takes place without the presence of Onsager-Feynman vortex lines. A rotating helium film has the advantage that it combines the simple geometry of bulk-liquid

experiments with critical velocities of the order of magnitude of 50 cm/sec.<sup>1</sup>

The interesting question is whether or not the film rotates with the surface on which it is formed. If the film is brought into motion, then the surface of the film should curve for the same reason that a classical liquid in a rotating bucket has a parabolic shape. For the film, however, the change in the surface is of the order of Angstroms instead of centimeters because the force field is not gravity