excitations the consequent increase in total energy is proportional to the number of excited electrons. This means that a finite energy is required to excite an electron from the ground state. The same applies to real excited $\mathbf{k}$, $-\mathbf{k}$ pairs. If $f(\epsilon)$ is the probability that a Bloch state of energy ϵ is occupied by an excited electron above the Fermi sea, and $1-f(-\epsilon)$ the probability that there is a hole below, one finds for the interaction energy an expression similar to (4) but with $[\Gamma(\epsilon)]^2$ replaced by $g(\epsilon)\{1-[f(\epsilon)]^2-g(\epsilon)\}$. For small excitations above $T=0°$K, the total pair energy may be expressed in the weak-coupling limit as

$$W=-\frac{n_c^2}{2N(0)}\left(1-\frac{4n_e}{n_c}\right), \quad n_e\ll n_c, \tag{12}$$

where n_c is the number of electrons in the virtually excited states at $T=0$ and n_e is the number of actually excited electrons. This leads to an energy gap[7] (i.e., the energy required to create an electron-hole pair):

$$E_G=\partial W/\partial n_e=2n_c/N(0) \quad \text{at} \quad T=0°\text{K}. \tag{13}$$

Taking the empirical $W=-H_c^2/8\pi$ and estimating $N(0)$ from the electronic specific heat, we find $E_G=k\times 13.8°$K for tin. This is to be compared with the experimental value of about $k\times 11.2°$K. Calculations are under way to determine the thermal properties at higher temperatures.

Advantages of the theory are (1) It leads to an energy-gap model of the sort that may be expected to account for the electromagnetic properties.[8] (2) It gives the isotope effect. (3) An order parameter, which might be taken as the fraction of electrons above the Fermi surface in virtual pair states, comes in a natural way. (4) An exponential factor in the energy may account for the fact that kT_c is very much smaller than $\hbar\omega$. (5) The theory is simple enough so that it should be possible to make calculations of thermal, transport, and electromagnetic properties of the superconducting state.

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Polarization of Nuclei by Resonance Saturation in Paramagnetic Crystals*†

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THE suggestion of Overhauser[1] that the saturation of the spin resonance of the conduction electrons in a metal should give nuclear polarizations of the order of $\beta H/kT$ (β=Bohr magneton, H=magnetic field) catalyzed thinking along these lines; it was soon realized by many[2] that related dynamic polarization processes are apropos to paramagnetic substances in general. In fact, even earlier, Pound[3] had produced enhanced populations by nuclear magnetic resonance saturation in a system with quadrupole splitting. Abragam[4] discusses the nuclear polarization obtainable by the saturation of the resolved paramagnetic resonance hfs lines in magnetically dilute crystals. In his scheme the strongly allowed electronic magnetic dipole transitions are saturated and the nuclear polarization is induced by suitable relaxation processes through the hfs coupling. We wish to point out that in many cases the saturation of certain so-called forbidden transitions will produce a comparable nuclear polarization directly in the sense that the applied radio-frequency field itself flips the nuclei. Such forbidden transitions are commonly observed in microwave paramagnetic resonance, e.g., in the case of appreciable nuclear quadrupole interactions and in cases where the nondiagonal magnetic hfs terms are not too small. As a specific sample of the latter, consider the following spin Hamiltonian,[5] appropriate for Co^{++} ions at low temperatures in a magnetically dilute axial crystal in an external magnetic field:

$$\mathcal{H}=\beta[g_{\parallel}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)+AI_zS_z+B(I_xS_x+I_yS_y)]+\mathcal{H}_{\text{relax}}+\mathcal{H}_{rf}.$$

The first two terms are the electronic Zeeman terms and are assumed to be much larger than the magnetic hyperfine terms in A and B. The energy levels are shown schematically in Fig. 1 where we have taken $A\simeq B$, $S=\frac{1}{2}$ and $I=2$, for illustration purposes. The various states are characterized in zero order by electronic and nuclear magnetic quantum numbers m and M, respectively. However, the term in B mixes the states so that to first order we have for the wave functions $\psi_a=\psi(\frac{1}{2},2)$, $\psi_b\cong\psi(\frac{1}{2},1)+(B/H_z)\psi(-\frac{1}{2},2)$, $\cdots$, $\psi_j\cong\psi(-\frac{1}{2},2)-(B/H_z)\psi(\frac{1}{2},1)$. The $\mathcal{H}_{\text{relax}}$ term gives relaxation transitions between the various states, the dominant ones being those shown for ($\Delta m=\pm 1$, $\Delta M=0$), corresponding to the electron spin-lattice relaxation. The $\Delta(m+M)=0$ relaxation transitions are considerably weaker, as are also those for ($\Delta m=0$, $\Delta M=\pm 1$), not shown. For simplicity the latter transitions are neglected; from reasonable assumptions concerning relaxation mechanisms it can be shown

that this may reduce the magnitude of the polarization calculated below by roughly a factor 2. The microwave field through the $\mathcal{H}_{rf}$ term induces the transitions ($\Delta m=\pm 1$, $\Delta M=0$) by the rf component perpendicular to H_z. These are the usual $2I+1$ paramagnetic resonance hfs lines. The rf component parallel to H_z induces the forbidden transitions $\Delta(m+M)=0$. These show up as $2I$ lines between the main lines. Let the rf field be polarized parallel to H_z and great enough to saturate the states b and j at resonance, i.e., make their populations equal. Then the unnormalized relative populations of the states are as shown in Fig. 1, where $2\delta=h\nu/kT$, and we have expanded the Boltzmann exponential, keeping only first order terms. The relatively small energy difference between adjacent M states is neglected. A similar situation occurs when the c and i levels are saturated, etc. Thus in general one expects $2I$ dc magnetic field values for which a fixed microwave frequency ν will induce a partial nuclear polarization. This polarization may be detected, for example, by observing the γ-ray anisotropy $\epsilon=1-g(0)/g(\pi/2)$ if the nuclei are radioactive. The relative magnitudes of the anisotropy lines can, in principle, uniquely determine the decay scheme. The lines form an antisymmetric pattern about their center point; this is due to the fact that the saturation of lines b and j, for example, give a population distribution which is inverted relative to that obtained by saturating e and g. As Abragam[4] points out, saturation of levels a and j will also give a nuclear polarization via the relaxation transitions b to j. The resulting anisotropy is of comparable magnitude and opposite in sign to that obtained by the direct saturation of levels b and j. The magnitude of the anisotropy depends on the decay scheme and is of order $\epsilon\sim(h\nu/kT)(2I+1)^{-1}$ for the saturation of a single line. This may be several percent at 3-cm wavelength and 1.5°K.

This method and related ones may be termed "high"-temperature dynamic polarization methods in contrast to the experiments of the Oxford and Leiden groups in which radioactive nuclei were first aligned by their static hfs at very low temperatures reached through adiabatic demagnetization.[6] In the latter experiments the polarizations and γ anisotropies obtained are considerably larger than those available by the method proposed here. However, larger activities and longer counting times may be used at the higher temperatures, so that comparable counting statistics may be obtained. The dynamic polarization method yields directly the spin and magnetic moment of the radioactive nucleus and, in fact, may be considered as a microscopic or quantum detector of magnetic resonance. As such, it is unique in that the signal is proportional to the number of decays instead of to the number of atoms as in magnetic resonance absorption, which is a macroscopic detector by contrast. Thus the polarization method is particularly appropriate for the determination of the hfs of short-lived nuclei. That the scheme proposed above will actually work has been demonstrated for 5.3-yr Co^{60}, as described in the following Letter,[7] and for 6-day Mn^{52}.[8]

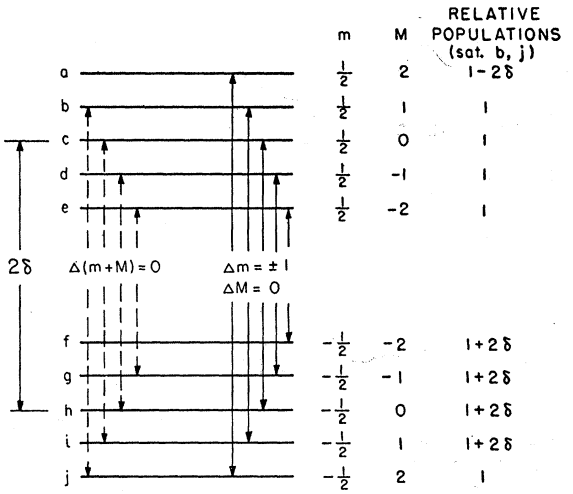

FIG. 1. Energy levels and transitions.

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γ-Ray Anisotropy of Co^{60} Nuclei Polarized by Paramagnetic Resonance Saturation*†

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THE proposal of Jeffries[1] in the preceding letter for the polarization of nuclei by the saturation of certain forbidden transitions in paramagnetic resonance has been successfully applied to 5.3-yr Co^{60} contained in a single crystal of $La_2Mg_3(NO_3)_{12}\cdot 24D_2O$.