Possible dynamic polarization of nuclei through the use of dielectric Van Vleck paramagnets

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Van Vleck paramagnets with a nonmagnetic ground state might be used to polarize nuclear spins. Thulium ethylsulfate is discussed as an example. The Stark structure of this compound is calculated for strong magnetic fields and resonant magnetic fields for intense lines of pulsed gas lasers in the submillimeter range. The possibility of transferring the polarization of the thulium nuclei to nuclei of liquid helium-3 is discussed. © *1995 American Institute of Physics.*

1. Systems with highly polarized nuclear spins are currently the subject of very active research in both particle physics and solid state physics.[1] Methods involving dynamic polarization of nuclei[1,2] are more accessible than "brute-force" methods (ultrastrong magnetic fields and ultralow temperatures). One method of dynamic nuclear polarization—the "solid effect"—is based on a transfer of polarization from paramagnetic impurity centers to the nuclear spin system. In the present letter we discuss a modification of this method which uses Van Vleck paramagnets, in which the Van Vleck ions are at the sites of a regular crystal lattice and act as paramagnetic centers in the transfer of polarization to nuclei.

2. The ground multiplet of crystals which contain rare-earth ions with an even number of electrons in the $4f$ shell (Pr^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}, and Tm^{3+}) is split by the crystal field, in such a way that the ground state becomes a singlet or nonmagnetic doublet split off from the higher-lying levels by a distance[3] $\Delta \approx 10-100$ cm^{-1}. The nuclear spins of Van Vleck ions and of diamagnetic atoms of the crystal lattice are effectively coupled to the electron cloud by a hyperfine interaction. An external magnetic field $\mathbf{H}_0$ induces a magnetic moment of the electron cloud in the nonmagnetic ground state. However, there can be no transfer of polarization from the electron cloud to nuclear spins at $kT \ll \Delta$ because of the static nature of the hyperfine field. The use of the solid effect in this situation thus means that the electron cloud must be put in an excited state (in this sense, it must be "depolarized"). During relaxation from this excited state, part of the electron polarization will be transferred to the nuclear spin system through a hyperfine interaction. If this path is to be taken, there are some obstacles to overcome. In the first place, since the energy interval between the ground and excited states of the ground term is fairly large, exciting the electron cloud will require the use of either laser light in the far-IR region[4] or ballistic heat pulses.[5] Second, there is a leakage of nuclear polarization as a result of nuclear spin–lattice relaxation. Let us discuss the latter factor in more detail.

Crystals of Van Vleck paramagnets contain paramagnetic impurities (Er^{3+}, Yb^{3+},

etc.). Fluctuations of the magnetic fields of these impurity ions give rise to a familiar mechanism of nuclear spin–lattice relaxation, which proceeds at a rate proportional to $1-p_0^2$, where p_0 is the polarization of the paramagnetic impurity. High magnetic fields must accordingly be used in order to reduce the loss which results from this relaxation mechanism.

In addition, the effective magnetic field at the nucleus of a rare-earth ion is the sum of H_0 and the hyperfine magnetic field $H_{\rm hf}$, which is directed parallel to the external field and which is stronger than it by a factor of α (the parameter α is called the "paramagnetic shift" and has a value in the interval 1–300). At temperatures $kT \ll \Delta$ the hyperfine magnetic field has both a constant component, which shifts the NMR frequency, and a fluctuation component, due to transitions of the $4f$-electron shell to excited states. The spectrum of thermal fluctuations of the hyperfine field has a nonzero component at the resonant frequency of the nuclear spins, ω_n, of both the Van Vleck ions and the diamagnetic atoms of the crystal lattice. As a result, an effective mechanism of nuclear spin–lattice relaxation comes into play.[6] For a nuclear spin $I=1/2$, the rate of this relaxation in a dielectric Van Vleck paramagnet is given, in the approximation of short correlation times for the fluctuations of the hyperfine fields, $\omega_n \tau_c \ll 1$ (τ_c is on the order of 10^{-10} s), by the expression[6] $T_1^{-1}=(A+B\omega_n^2)\exp(-\Delta/kT)$, where the parameters A and B are determined by the structure of the crystal lattice. This mechanism is predominant at temperatures of 1–2 K at concentrations on the order of 0.1% of the paramagnetic impurity. In strong magnetic fields, the effectiveness of the relaxation due to fluctuations of the hyperfine fields also falls off.

3. The use of strong magnetic fields (>50 kOe) also changes the intervals between the Stark-structure levels of Van Vleck ions (Sec. 4). This is an exceedingly important circumstance from the experimental standpoint, since it means that we can use a magnetic field to make the energy distance between the ground level and the excited level equal to the energy of some laser output line.

In order to monitor the possibility of a dynamic nuclear polarization using Van Vleck paramagnets, however, we need information on ESR in these strong magnetic fields. So far, an ESR has not been observed on transitions between a nonmagnetic ground state and the nearest excited state.

4. Let us illustrate the possibility of using the method of dynamic nuclear polarization involving Van Vleck paramagnets in the example of the well-studied crystal thulium ethylsulfate,[3] $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$ (TmES). Figure 1 shows the Stark energy levels of the Tm^{3+} ion [with a $^3H_6$ ($J=6$) ground term] versus the magnetic field H_0, directed perpendicular to the c crystallographic axis. At liquid-helium temperatures the magnetic properties of the ions are determined by the lower levels: by the nonmagnetic singlet $|g\rangle$ and by the first excited doublet $|d_{1,2}\rangle$, which is split by the strong magnetic field (Fig. 2). Here is a list of the possible magnetic transitions along with the squares of the corresponding matrix elements (the matrix elements for transitions $|g\rangle \rightarrow |d_1\rangle$ in magnetic fields up to 250 kOe):

For the $9R30$ submillimeter-range line, with a frequency of 43.3 cm^{-1}, of a laser using gaseous methyl fluoride, CH_3F, at a pulse power of 10 400 μJ (Ref. 4), the resonant

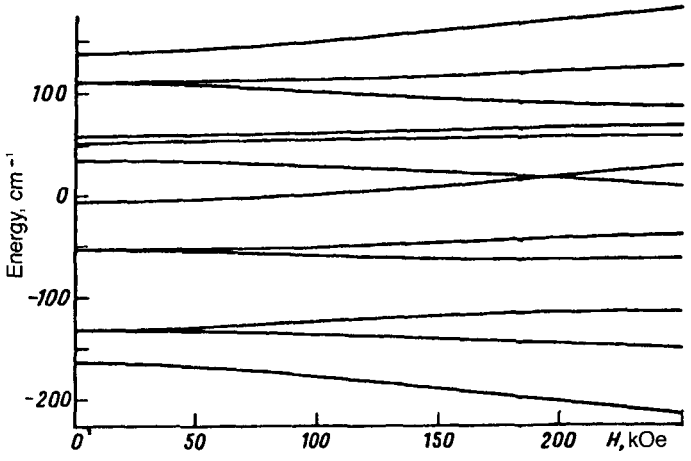

FIG. 1. Stark energy levels of the Tm^{3+} ion [$^3H_6$ ground term ($J=6$)] in thulium ethylsulfate versus the strength of the external magnetic field, which is directed perpendicular to the c crystallographic axis.

field for the transition $|g\rangle \rightarrow |d_2\rangle$ is 63.97 kOe, and the square of the matrix element is $|\langle g|J_x|d_2\rangle|^2 = 10.8$.

For the $9R26$ line (39.9 cm^{-1}, 9500 μJ) the field is 53.16 kOe, and the square of the matrix element is $|\langle g|J_x|d_2\rangle|^2 = 12.5$.

For the $9R34$ line (46.6 cm^{-1}, 5800 μJ), the numbers are 73.44 kOe and $|\langle g|J_x|d_2\rangle|^2 = 9.6$.

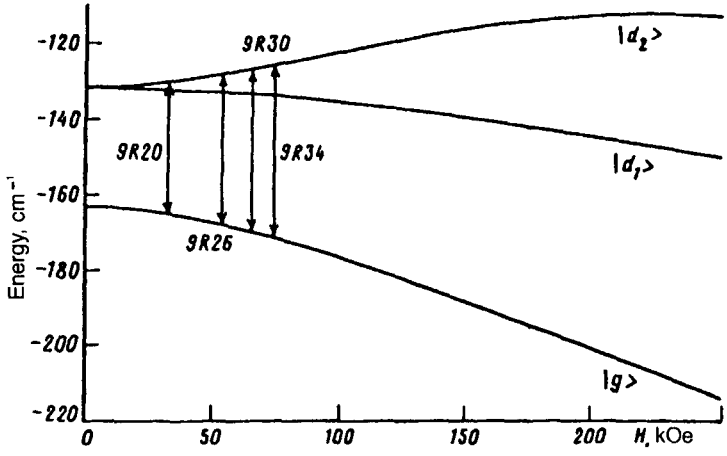

FIG. 2. Low-lying energy levels of the Tm^{3+} ion in thulium ethylsulfate in strong magnetic fields, along with possible ESR transitions in the submillimeter range (see the text proper for an explanation).

For the $9R20$ line (34.7 cm^{-1}, 5700 μJ), the numbers are 32.43 kOe and $|\langle g|J_x|d_2\rangle|^2 = 16.0$.

The ESR line corresponding to the transition $|g\rangle \rightarrow |d_2\rangle$ obviously has a hyperfine structure consisting of two lines (material consisting of 100% of the isotope ^{169}Tm has a nuclear spin $I = 1/2$). The first step toward realization of the method proposed here should be to observe an ESR involving Tm^{3+} ions in strong magnetic fields (>50 kOe). In contrast with the ordinary solid effect, for which saturation of the ESR line of paramagnetic impurity centers occurs in the wing, the saturation in our case should occur at one component of the hyperfine structure. Furthermore, the method proposed here does not require the satisfaction of conditions on the relation between the ESR linewidth of the paramagnetic centers and the resonance frequency of the nuclear spins.[1,2]

5. When the nuclear polarization of thulium is detected in this case, one should bear in mind that the paramagnetic shift with increasing applied magnetic field H_0 decreases because of an increase in the splitting of the ground level and the excited level.

The polarization of the thulium nuclei could be transferred to other nuclei of diamagnetic crystal atoms, since the effective gyromagnetic ratio of the ^{169}Tm nuclei depends on the orientation of the magnetic field,[3] and a cross relaxation occurs in certain orientations. In this case the nuclei of liquid helium-3 in contact with the crystal surface of a Van Vleck paramagnet do not differ in any fundamental way from the nuclei of diamagnetic atoms discussed above. As a result of the transfer of magnetization which has been demonstrated by Richardson *et al.*,[7] the polarization of thulium nuclei could be transferred to nuclei of helium-3 adsorbed on the surface of a crystal and then to the nuclei of liquid helium. This process would be most effective under the conditions of the resonant magnetic coupling observed in Ref. 8.

6. Again, we would like to stress the need to use strong magnetic fields. On the one hand, nuclear spin–lattice relaxation is essentially frozen in this case. On the other hand, strong magnetic fields are required to create the resonant conditions for the ESR of Van Vleck ions.

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