Slowing down of nuclear spin-lattice relaxation in molecular crystals exposed to light

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A strong slowing down of nuclear spin-lattice relaxation has been observed in molecular crystals illuminated in magnetic fields at 4.2°K. The effect is attributed to a photochemical reaction in which triplet states take part.

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It is known that illumination of certain molecular crystals by unpolarized light leads to optical polarization of the nuclei (OPN).[1] In a study of this effect at $T = 4.2$ °K, we have observed an unexpected and rather interesting phenomenon, namely, after turning off the optical pumping causing the OPN, the proton spin-lattice relaxation time (T_1) turns out to be much longer than prior to the illumination.

Thus illumination, by a DRSh-500 lamp for one hour, of a fluorine crystal ($C_{13}H_{10}$) with approximately 0.1% of o-phenanthroline ($C_{14}H_8N_2$) in the absorption band of the first singlet-singlet transition of the impurity (300–350 nm) led to an increase of T_1 in a magnetic field H_0 =3300 Oe from 70 min to 8 hr, and after illuminating the same crystal for 2.3 hr the time T_1 reached 40 hr(!). The slowing down of the spin-lattice relaxation turned out to be not connected with the OPN effect; this is evidenced by the fact that the increased value of T_1 was preserved also after the nuclear polarization returned to equilibrium with the lattice. The initial properties were acquired by the sample only as a result of "annealing" for several minutes at a temperature not lower than 40 °K; after these procedures, the time T_1 at 4.2 °K decreased to its usual value. Similar results were obtained also with other crystals, namely fluorine with anthracene impurity and diphenyl with $\alpha\alpha$-dipyridyl impurity.

To explain the nature of the effect, it is important to know the mechanism of nuclear spin-lattice relaxation. Estimates show[2] that the internal motions in fluorine at 4.2 °K lead to values of T_1 not lower than 80 hr (at
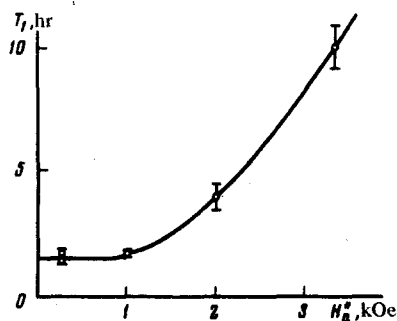

Dependence of the spin-lattice relaxation time of protons in a fluorine crystal on the magnetic field in which the sample is located during the illumination (the illumination time was 1 hr, T_1 was measured in a field 3300 Oe).

$H_0 = 3300$ Oe). On the other hand, the experimental dependence of T_1 on H_0 obtained by us at 4.2 °K in the range from 100 to 5000 Oe was of the form $T_1 \propto (H_0)^{3/4}$ both before and after the illumination, and this form is typical of relaxation via a paramagnetic impurity.[3] Thus, the cause of the growth of T_1 is apparently the decrease of the concentration of the paramagnetic centers under the influence of the light.

The most probable uncontrollable paramagnetic impurity in aromatic molecular crystals is molecular oxygen. The role of oxygen is confirmed by the fact that when the ampule with the melt is filled with air during the growth of the crystal the initial value of T_1 (prior to illumination) is decreased by a factor 1.5–2, whereas the influence of the illumination on T_1 remains the same as before.

The mechanism whereby the paramagnetic centers are annihilated by illumination may be the onset of a chemical bond between the oxygen molecule and the aromatic molecule of the matrix, which is in an excited triplet state (these metastable states can become populated by the transfer of excitation from the first excited singlet of the impurity[4]). The resultant complex molecule will be diamagnetic; the activation energy for its decay, as follows from experiments with "annealing," is approximately 30 cm^{-1}. The role of triplet states in the described mechanism of the reaction is confirmed by the fact that the magnitude of the effect depends strongly on the field H_0^* in which the sample was located during the time of illumination (see the figure). It is seen from the figure that the reaction becomes effective at $H_0^* \gtrsim 1000$ Oe, corresponding to the initial splitting of the triplet state of the fluorine molecule,[5] i.e., the region in which the makeup of the wave functions of this state changes abruptly. A similar photochemical reaction was observed at room temperature in tetracene films.[6]

We note in conclusion that the observed effects can be regarded as a rather effective method of ridding crystals of ferromagnetic impurities; it suffices to state that the fluorine crystals employed by us were first purified by a hundredfold zone melting in vacuum and contained, according to estimates, not more than 10^{12} cm^{-3} oxygen molecules.

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