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DISCRETE SATURATION OF INHOMOGENEOUSLY BROADENED EPR LINES

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Discrete saturation of inhomogeneously broadened EPR lines is detected, for which the hyperfine structure due to the nuclei surrounding the paramagnetic center can be resolved. Saturation of the EPR line is accomplished by means of narrow, single microwave pulses 1 to 50 μsec long. The phenomenon of discrete saturation was observed for paramagnetic ions in an ionic crystal, for F centers, and also for free-radical EPR lines.

We have investigated the relaxation processes in EPR lines in single crystals of CaF_2, SrF_2, and BaF_2 containing U^{3+} as an impurity in tetragonal surroundings at a concentration of 0.1 to 0.15%, in F centers in LiF with a concentration of 10^{17} cm^{-3}, and also in lines due to free radicals in neutron-irradiated teflon and polyethylene. The spin-lattice relaxation time T_1 for these various samples varied from 10^{-3} to 10 sec at liquid-helium temperature.

The width of the EPR lines in our samples was due to the interaction of the paramagnetic center with surrounding nuclei (in the case of teflon there was an additional anisotropic broadening). The superhyperfine structure (shfs) of the lines is resolved only at certain orientations of the magnetic field relative to the crystal symmetry axis. Short, single saturating pulses enhance the resolution of the shfs in the EPR lines. Moreover, at orientations in which the shfs is not observed, application of a saturating pulse leads to resolution of the structure.

As Portis has shown,[1] saturation of an EPR line by narrow microwave pulses can lead to the appearance of a hole in the line, if it is inhomogeneously broadened, or to saturation of the entire EPR line in the case of homogeneous broadening. This mechanism of saturation of EPR lines does not apply to our case, which in principle can be described as an intermediate one.

It is possible that the discrete saturation of an EPR line that we have observed has the same origin as the process of "discrete spin diffusion" observed by Feher and Gere,[2] who studied the relaxation processes of the donor impurity arsenic in silicon at a concentration of 2×10^{16} cm^{-3}. It was found that saturation of the central portion of the line by a microwave pulse longer than 10 sec (the spin-lattice relaxation time in this sample was several hours at 1.25°K), in addition to depressing the line at the center, also produced side depressions at distances corresponding to the Larmor precession frequencies of Si^{29} nuclei located at different lattice sites. This phenomenon was attributed by the authors to a particular kind of spin diffusion, the so-called "discrete spin diffusion." However, as will be shown below, in our experiments the discrete saturation of the EPR line is an induced process which takes place under the influence of and during the action of a saturating microwave pulse. Hence the term "spin diffusion" seems to us to be inappropriate for the description of these processes.

EXPERIMENTAL METHOD

We used a superheterodyne spectrometer working at 3.2 cm at liquid-helium temperatures, with an additional klystron with a power output of several hundred milliwatts for the pulsed saturation of the EPR line.

A sinusoidal voltage at line frequency (50 Hz) was used to modulate the magnetic field. Synchronization of the saturating pulse with the magnetic field scan was accomplished with a Ps-64M scaling circuit, to the input of which a sinusoidal voltage from the line was connected through a phase shifter. The output pulses from the scaling circuit started a GIP-2M square-wave generator, which pulsed the klystron.

The microwave pulses we used were 1 to 50 μsec in length. Pulses of length greater than 50 μsec, for the given rate of magnetic field sweep (50 Hz) worsened the effect of displaying of hyperfine structure (hfs).

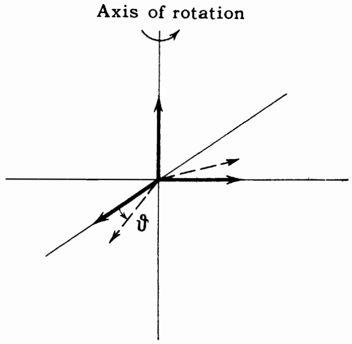

FIG. 1. Schematic representation of the mutually perpendicular symmetry axes of the three unequivalent U^{3+} ions in CaF$_2$.

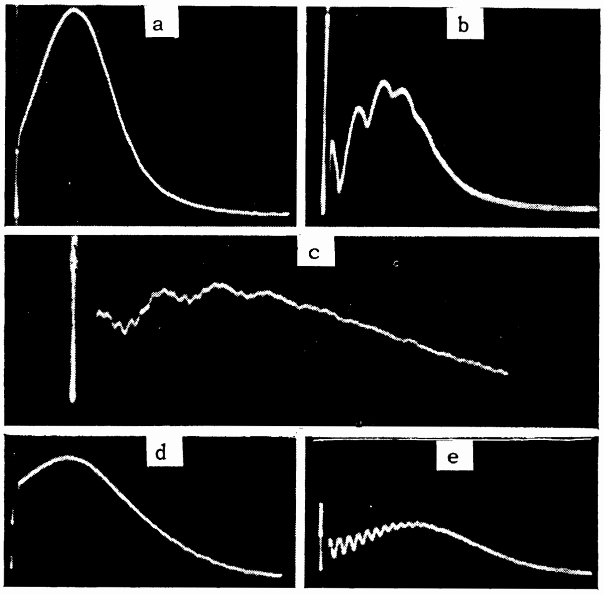

FIG. 2. Discrete saturation of the EPR line of U^{3+} in SrF$_2$: a, b–$\theta = 2°$; c–$\theta = 5°$; d, e–$\theta = 15°$. In a and d there is no discrete saturation of the line because the saturating pulse was attenuated by 40 dB.

EXPERIMENTAL RESULTS AND DISCUSSION

The paramagnetic resonance of U^{3+} in CaF$_2$, SrF$_2$, and BaF$_2$ in tetragonal symmetry has been studied before.[3,4] The EPR spectra are explained as due to three inequivalent ions with mutually perpendicular symmetry axes along the principal axes of the cubic CaF$_2$ lattice. If one cuts a single crystal of fluorite such that the symmetry axis of one of the inequivalent ions lies along the axis of rotation (see Fig. 1), which makes a right angle with the magnetic field, then when the crystal is rotated, the EPR line belonging to this type of U^{3+} ion remains stationary with g factor $g_\perp$. At the same time, the two lines belonging to the other two types of inequivalent ions pass successively through g values from $g_\parallel$ to $g_\perp$. When one of the principal axes of the cube is directed along the magnetic field, two EPR lines are observed in the spectrum, since two kinds of inequivalent ions have their symmetry axes at right angles with the field H.

The hfs due to the nuclei of the F^- ions surrounding the paramagnetic ion was studied in[3,5].

The shfs is resolved in the paramagnetic resonance lines only in orientations corresponding to g values $g_\parallel$ and $g_\perp$ for U^{3+} in CaF$_2$, SrF$_2$, and BaF$_2$, and only for U^{3+} in CaF$_2$ is it slightly resolved also at several other orientations.

Figure 2a shows an oscillogram of the EPR line of U^{3+} in SrF$_2$ at an orientation for which the magnetic field is almost perpendicular to the symmetry axes for two kinds of unequivalent ions. The angle θ (see Fig. 1) was 1—2°. Because of the superposition of the fluorine hfs from the two unequivalent ions, the structure is not resolved. The oscillograph driven sweep was synchronized with the saturating pulse, which in this case was attenuated by 40 dB and did not affect the EPR line in any way.

In Fig. 2b is shown the same line when the microwave saturating pulse was not attenuated. It is seen that the fluorine hfs, which corresponds to the resolved hfs at perfect orientation ($\theta = 0°$), is now resolved. It should be noted that at $\theta = 0°$ the hfs spectrum is better resolved when the microwave pulse falls between the shfs components and is worsened when it occurs at the maximum of one of the lines.

Figure 2c shows an oscillogram of the same line at the angle $\theta = 5°$. In this case the EPR lines of the two unequivalent ions are separated, and the fluorine hfs is not resolved. The action of a narrow saturating pulse resolves it. The envelope of this structure coincides with the spectrum observed at the orientation $\theta = 0°$; however, as is seen from the oscillogram, an additional structure appears in the line.

The next oscillogram (Fig. 2d) shows the EPR line at $\theta = 15°$. The power of the saturating pulse was attenuated by 40 dB. Figure 2e shows the same line after the saturating pulse is applied without attenuation.

We have observed an analogous pattern of discrete saturation with resolution of shfs in other kinds of samples as well. In particular, we investigated F centers in LiF at a concentration of 10^{17} cm^{-3} and the anisotropically broadened line of the free radicals in neutron-irradiated teflon and polyethylene. The discrete saturation in the EPR lines of the F center and of teflon is shown in Figs. 3 and 4.

The width of propagation of discrete saturation over an EPR line depends on the direction of the magnetic field. For example, for U^{3+} in SrF$_2$ it

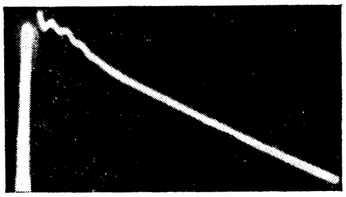

FIG. 3. Discrete saturation in a portion of the EPR line of the F center in LiF. The width of propagation of the holes in discrete saturation is in this case limited by the time T_{21} for the given rate of scan of the magnetic field.

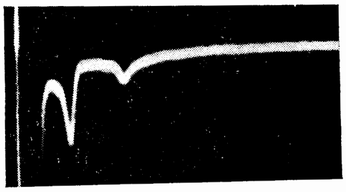

FIG. 4. A portion of the EPR line of the free radical in neutron-irradiated teflon. The first hole in the line is caused by the direct action of the pulse from the saturating klystron, whose frequency was shifted relative to the frequency of the signal klystron.

varies by approximately a factor of two for different orientations of the magnetic field. As the saturating power is reduced, discrete saturation in the line is gradually weakened, while its propagation width remains almost unchanged. We investigated the dependence of the discrete saturation on the length of the microwave pulse and on its power. The length t of the pulses in this case varied from 3 to 30 μsec, and the power P over a hundredfold. It was found that the saturating pulse had the same effect if the product Pt (the pulse energy) was unchanged.

Before discussing the mechanisms which might lead to this discrete saturation, we shall show that these processes develop under the influence of the saturating microwave pulse during the time that it acts.

Actually, a study of the relaxation processes in the EPR lines of U^{3+} in fluorides shows that when the lines are saturated by short pulses, the curves of signal reduction consist of two exponentials with a short and a long characteristic time T_{21} and T_1, corresponding to spin-spin cross-relaxation processes inside the line and spin-lattice relaxation. It has been established that refilling of the holes caused by discrete saturation in the line occurs in a time equal to T_{21}. Naturally, in order to see discrete saturation it is necessary to traverse the line or a specified part of it in a time $\tau < T_{21}$. Let us now assume that the discrete saturation we have observed is a process of discrete spin diffusion. Then in order to observe holes in the line, the characteristic time of discrete diffusion T'_{21} should be shorter than τ. From this it follows that $T'_{21} < T_{21}$.

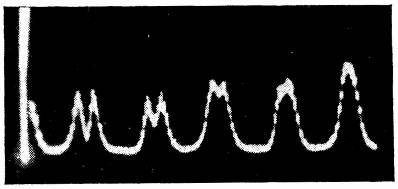

FIG. 5. EPR line of U^{3+} in SrF_2, in the orientation $\theta = 0$, and with g factor equal to $g_{||}$. The microwave pulse yields a wide hole in the line, which is then refilled in time T_{21}.

This assertion contradicts many experimental facts. For example, Fig. 5 shows an oscillogram of the EPR line of U^{3+} in SrF_2 in parallel orientation ($\theta = 0$) with the value of the magnetic field corresponding to $g_{||}$. In this orientation the line has a resolved fluorine hfs. The action of a saturating pulse leads to discrete saturation which encompasses approximately ⅔ of the line width. As was indicated above, the width of discrete saturation does not depend on the magnitude of the power. Increasing the power and also the length of the pulse up to 300 μsec easily forms a hole in the line, the width of which on the time scale is several times greater than the length of the saturating pulse. However, on account of its relatively long length, the discrete saturation is not resolved. As measurements have shown, refilling of this hole takes place in a time T_{21}, which is completely inexplicable from the point of view of the concept of discrete spin diffusion, according to which the nonequilibrium state in the central portion of the line should have been filled in a time shorter than T_{21}. This contradiction is direct proof that the discrete saturation is not a diffusion process but an induced process taking place during the time that the saturating pulse acts.

Let us consider the mechanisms which might lead to discrete saturation in an EPR line. We shall assume that the width of a line with unresolved shfs is due to the nuclei surrounding the paramagnetic center. We represent the energy levels as a set of subsystems shifted relative to one another, and for simplicity we assume that the levels are equidistant within a subsystem. Figure 6 shows a subsystem of equidistant energy levels. Here m is the projection of the electronic spin, and M is the projection of the total spin of the nearest-neighbor nuclei. In order that discrete saturation should occur, we shall assume that the saturating pulse opens up "horizontal" paths in the levels, which are indicated by arrows. It is easy to see that if one "heats" the pair of levels

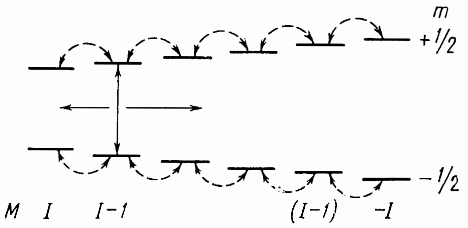

FIG. 6. Subsystem of equidistant nuclear levels. The solid horizontal arrows indicate the propagation of "heat" in the spin system, if one admits the existence of "horizontal" paths in the levels, during the action of a microwave pulse (the "horizontal" paths are indicated by dashed arrows).

indicated by the vertical arrow in Fig. 6 with a saturating pulse, then, owing to the presence of the horizontal paths, the "heat" will pass over to the neighboring levels during the time that the pulse acts. Thus, one will observe discrete saturation of the EPR line.

The elucidation of the actual mechanism responsible for this opening up of horizontal paths in the system of sublevels while a saturating microwave pulse is acting is a complex problem that we have not completely solved. However, the mechanism illustrated in Fig. 7 is a most likely one. Actually, as Clogston et al. have shown,[6] in the general case, along with the transitions $\Delta m = \pm 1$ and $\Delta M = 0$, transitions with $\Delta m = \pm 1$ and $\Delta M = \pm 1$ may have a non-zero probability. This is due to the fact that the direction of the magnetic field

$$H_i = H_0 n_i + \frac{m}{\gamma \beta_N} A_{ik} n_k \qquad (i, k = x, y, z)$$

at the nucleus changes with a change in m. This is because of a change in direction of the second term in H, which in general does not coincide with the direction of n (where n is a unit vector along H_0, A_{ik} is the hyperfine interaction tensor).

In Fig. 7 the solid arrows indicate saturation of the "forbidden" transition $\Delta M = \pm 1$ and $\Delta M = \pm 1$. In such transitions the projections of the spin of the electron and of one of its neighboring nuclei change simultaneously.

Let there now be a transition in which at a given paramagnetic center only the electron spin projection changes with a simultaneous re-orientation of a nuclear spin situated in the immediate vicinity of a neighboring paramagnetic center. It is assumed that the latter has the given subsystem of levels. These transitions are indicated by dashed arrows in Fig. 7. In principle such transitions can be accomplished via the electronic spin-spin interaction of neighboring paramagnetic centers.

It is possible to think of another mechanism for this phenomenon of discrete saturation. The microwave pulse power evokes saturation of a certain spin packet in the line. Then the saturation is propagated into the wings of this spin packet in a time T_2. An estimate of this time in the case of U^{3+} in fluorides based on the measured value of T_{21} and the half-width of the whole line gives 10^{-7} sec, which is much less that the length of the saturating pulse. The wings of the saturated packet will encompass a significant portion of the EPR line width and will saturate it homogeneously. In the background of homogeneous saturation the holes of discrete saturation observed in the EPR line represent portions of "easy" saturation, which may be due to the predominant transfer of energy to those packets of the EPR line which belong to the subsystem of levels of the saturated spin packet.

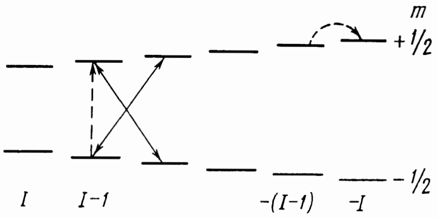

FIG. 7. Illustration of a possible mechanism for the opening up of "horizontal" paths by a microwave pulse. In addition to the transitions ($\pm 1/2$, M) → ($\pm 1/2$, M ±1), which are indicated by the solid arrows, the transition ($-1/2$, M) → ($+1/2$, M) is shown, which is accompanied by a simultaneous reorientation of the spin of a nucleus located in the immediate vicinity of a neighboring paramagnetic ion, thus maintaining energy conservation.

CONCLUSION

Processes of discrete saturation of inhomogeneously broadened EPR lines explain certain poorly understood phenomena that we have observed in investigating the relaxation processes of U^{3+} in fluorides. This concerns first of all the weight of the cross-relaxation process in the curve of signal re-establishment. In our experiments the weight of the cross-relaxation portion of the exponential varied widely; nevertheless, its average value was about 50%. If one starts from the Portis mechanism for the saturation of an inhomogeneously broadened line, the weight of the cross-relaxation process with a short time T_{21} should be about 100% with saturation of the line by narrow pulses. Actually, the heat capacity of the narrow packet saturated by a pulse is much less than that of the rest of the line, and if cross-relaxation processes do occur the weight of these processes ought to predominate in the relaxation curve, which is not confirmed by experiment. This experimental fact is easy to explain if one takes processes of discrete saturation into consideration.

In conclusion, it must be mentioned that the method of discrete saturation can be applied to the study of structure in EPR lines in which shfs is not resolved.

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