ENDOR SPECTRUM AND WAVEFUNCTION FOR THE RELAXED-EXCITED STATE OF THE F CENTER IN KBr

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Résumé. — La densité de probabilité radiale de l'Etat Excité Relaxé (RES) du centre F dans KBr a été déduite de mesures de fréquences hyperfines.

Les résultats ne permettent pas de choisir entre les états $|2s\rangle$ et $|2p\rangle$. Cependant, la densité de probabilité expérimentale peut être assez bien représentée par un état diffus $|2p\rangle$ omettant la dépendance angulaire.

Abstract. — The radial probability density of the Relaxed Excited State (RES) of the F center in KBr has been extracted from measured hyperfine frequencies.

The results do not allow statements to be made about the model of $|2s\rangle$ versus $|2p\rangle$ state. However the experimental probability density can be represented fairly well by a diffuse $|2p\rangle$ state lacking the angular dependence.

1. General considerations and previous results. — Recently L. F. Mollenauer and coworkers have been able to detect for the first time the ENDOR resonance in the relaxed-excited state (RES) of the F center in KI [1], [2]. The most difficult and fundamental problems result from the short lifetime τ of the RES. Indeed in order to affect the F center optical cycle [3] the electron has to « feel » the nuclear reversal during its stay in the RES. Hence the nuclear direction must be reversed in a time shorter than τ . Owing to the fact that the linewidth of the nuclear resonances is practically determined by the short lifetime τ , the last condition becomes :

$$(I + m)(I - m + 1)(\gamma_n H_1 \tau)^2 \geq 1 \quad (1)$$

where γ_n is the gyromagnetic ratio of the nuclei and H_1 is one half the amplitude of the oscillating rf field, $H_{rf} = 2 H_1$. We have used in (1) the normal transition probability from the state m to $m - 1$ for a system of nuclear spins with angular momentum I . We disregarded completely the enhancement of the nuclear transition probability [4] which occurs in the presence of an hyperfine interaction. Hence the condition (1) is more restrictive than the true one. Keeping this in mind we will use the sign equal in (1) from now on.

In general a field H_{rf} of the order of 100 Oe and at a frequency of several tens of MHz is necessary to satisfy the (1) in a typical ENDOR experiment. The problem of generating such high H_{rf} was solved by Mollenauer *et al.* [2] by using an ingenious experi-

mental arrangement. We will not describe here the apparatus, which was done elsewhere, but we will be content to say that the rf field is generated by two loops of copper wire, $\varnothing \simeq 0.2$ mm, which enclose an area of ~ 1 mm². From (1) we calculate $H_{rf} = 50$ Oe for F center in KI, $\tau = 3.2 \times 10^{-6}$ s [5]. This implies at 30 MHz and at the liquid helium temperature a power dissipation by the loop of 8 mW. Now because of the Kapitza resistance [6] the temperature of the copper wires is ~ 0.7 K higher than the bath temperature, $T_0 = 1.7$ K. It is clear that in such conditions the system is highly unstable. Much worse is the situation for F center in KBr where $\tau = 2 \times 10^{-6}$ s [7]. In this case $H_{rf} = 100$ Oe and the power dissipation is 30 mW, which brings the temperature of the loop ~ 2.5 K higher than the bath. This means that if we use the maximum experimentally acceptable H_{rf} for both KI and KBr crystals, the signal to noise ratio is much worse in KBr than in KI.

The ENDOR spectrum of F center in KI revealed with this apparatus is fairly good and the hyperfine frequencies are so well resolved that we were able to extract from them the radial probability density for the RES [8]. In the case of KBr another difficulty has to be considered. The ENDOR spectrum contains two spectra due to the isotopes Br^{79} ($I = \frac{3}{2}$, $g\mu_B/h = 1\,066.7$ Hz/G, $\sim 50\%$ natural abundance) and Br^{81} ($I = \frac{3}{2}$, $g\mu_B/h = 1\,149.9$ Hz/G, $\sim 50\%$ natural abundance); g is the nuclear spectroscopic splitting factor and μ_B is the Bohr magneton. Nevertheless we succeeded in detecting the ENDOR spec-

trum in KBr [8]. As expected the spectrum was not resolved and the identification of the hyperfine frequencies was almost impossible. Only the maximum hyperfine frequency was extracted from it, i. e.

$$(v_{\text{hf}})_{\text{max}} \simeq 11.8 \text{ MHz}.$$

If $P(\rho_i)$ is the electron probability density at the nuclear site i , where ρ is expressed in units of the nearest-neighbor distance $d = 3.298 \text{ \AA}$ for KBr, the hyperfine frequency is given by :

$$(v_{\text{hf}})_i = CAP(\rho_i) \quad (2)$$

where A is the amplification factor and C is 2.319 2 MHz for Br^{79} and 2.500 1 for Br^{81} . Assuming as for F center in KI that the ESR linewidth is due to hyperfine broadening, we have :

$$\Delta H = 2.020 \left\{ 0.5 \left[\sum_i (v_{\text{hf}})_i^2 \right]^{1/2} + 0.5 \left[\sum_j (v_{\text{hf}})_j^2 \right]^{1/2} \right\} \quad (3)$$

where ΔH is the full width at half power points of the ESR line of the RES and the sums over i and j refer to the isotopes Br^{79} and Br^{81} respectively. Since the nuclear Zeeman frequencies at the magnetic field used are $\nu_Z = 21.52 \text{ MHz}$ (Br^{79}) and $\nu_Z = 23.20 \text{ MHz}$ (Br^{81}) and the ENDOR frequencies are given by $\nu_E = \nu_Z + \nu_{\text{hf}}$, the maximum hyperfine frequency measured refers to the Br^{81} isotope. Assuming as for

the RES of F center in KI a pure $|2p\rangle$ state without angular dependence :

$$P(\rho) = \left(\frac{\eta^3}{3\pi} \right) (\eta\rho)^2 \exp(-2\eta\rho) \quad (4)$$

and taking in account the experimental value of the ESR linewidth $\Delta H = 270 \text{ Oe}$, we obtain, from (2) and (3), $\eta \simeq 0.48$ and $A \simeq 3000$ for the RES of F center in KBr.

2. Actual results. — The method followed in the previous section to calculate the values of η and A is highly unsatisfactory. First of all we used only one feature of the ENDOR spectrum, i. e. $(v_{\text{hf}})_{\text{max}}$, without matching the electron probability density $P(\rho)$ to the whole spectrum. Secondly, the experimental value of $(v_{\text{hf}})_{\text{max}}$ is approximated within $\sim 10\%$ which reflects on η and A .

For these reasons we tried to extract more information from the experimental ENDOR spectra. Indeed we obtained several spectra relative to different samples, always hoping to get a good one, which was never the case. Later we analysed these spectra more carefully taking the mean value of 12 (twelve) of them point by point. In this manner the S/N ratio is expected to improve by a factor $\sim \sqrt{12} = 3.5$. In figure 1a, solid curve, the ENDOR spectrum so

FIG. 1a. — Experimental ENDOR spectrum (solid curve) compared with computer simulation (dashed curve). Theoretical ENDOR spectrum due to Br^{79} b) and Br^{81} c). The numbers besides the dashed curves are the numbers n_s of equivalent nuclei which are responsible of that portion of curve.

obtained is displayed versus ν_E and ν_{hf} . Obviously it is not structured like the similar spectrum of KI [1] but it has enough peaks at 35, 32.3, 30.5 and 28.5 MHz to make possible a theoretical fitting.

We made a computer simulation of this spectrum based on the theoretical hyperfine frequencies (2) and with linewidths adjusted for a best fit. As expected the linewidths used here are larger than those previously used for KI [8]. Each normalized line was multiplied by an intensity factor

$$n_s \nu_E^2 \{ 1 - \exp[-(\nu_{hf}/\Delta)^2] \},$$

$\Delta = 5$ MHz to reflect the dependence on the number of equivalent nuclei, n_s , in each shell, to reflect the fact that the probability for flipping a nuclear spin goes as ν_E^2 , and to reflect the fact that cross-relaxation effects tend to short-circuit the ENDOR at low value of ν_{hf} . The best fit is shown in figure 1a, dashed curve. To obtain this fit we shifted practically only one frequency clearly indicated in figure 2, circles, where the

FIG. 2. — Probability density $P(\rho)$ versus units of the lattice parameter $d = 3.298$. Solid curve is eq. (4) for $\eta = 0.48$. The dots and circles represent the frequencies used in the computer simulation. The number besides each dot or circle is the number n_s of equivalent nuclei of the halides shell.

hyperfine frequencies, dots, for Br^{71} and Br^{81} are reported. The solid line represents the function $P(\rho)$ and the number besides each dot or circle represents the number n_s of equivalent nuclei in each shell. In figure 1b and 1c the separate spectra of ENDOR for Br^{79} and Br^{81} are given; the sum of the two gives the dashed line in figure 1a. The fit is obtained with $\eta = 0.48$ and $A = 2990$, values similar to the previous ones obtained using only the maximum hyperfine frequency. However these values are now more reliable and the uncertainty upon them is much smaller. For example a variation of 0.01 in the value of η makes the fitting almost impossible.

The RES radiative lifetime, $\tau = 2 \times 10^{-6}$ s, implies for the squared transition matrix element, $|x|^2$, a value between $0.0076 d^2$ and $0.0110 d^2$, the two limits obtained with and without local field correction. But $|x|^2$ is also given by :

$$|x|^2 = |\langle 1s | x | 2p \rangle|^2 \quad (5)$$

where $|2p\rangle$ is the RES wavefunction, whose probability density is given by (4) and $|1s\rangle$ is the wavefunction for the non-relaxed ground state. We take the expression proposed by Fowler [9] for F center in NaCl :

$$|1s\rangle = \frac{\alpha^{3/2}}{7\pi^{1/2}} (1 + \alpha r) e^{-\alpha r}. \quad (6)$$

Using (6) and (4) in (5) we obtain :

$$|x|^2 = \frac{1}{3} \frac{32^2}{7} \frac{\alpha^3 \eta^5 (\eta + 6\alpha)^2}{(\alpha + \eta)^{12}} d^2. \quad (7)$$

In order to remain in the interval of $|x|^2$ implied by the lifetime τ , α has to vary between 2.23 and 2.09. These numbers are respectively $\sim 3\%$ and $\sim 9\%$ smaller than the value used by Fowler for NaCl.

The aim of this work was to test the reliability of the model which assigns to the RES of F center a very diffuse 2p-like [9], [10] wavefunction, in contrast with the very compact one for the ground state. The model was used successfully to explain the ENDOR spectrum in KI [8] and now, applied to the more complicated case of KBr, it gives a satisfactory agreement with the partially resolved ENDOR spectrum.

In conclusion we can say that at least for KI and KBr no doubts remain on the diffuse wave function of the RES of F center. (See note added.)

We would like to acknowledge the constant support given us by C. D. Jeffries, Professor at the Physics Department of the University of California, Berkeley, where the experimental part of this work was done. Also we are indebted with Alvaro Di Salvo for the useful assistance with the computer calculation.

Note added. — Following completion of this manuscript, W. B. Fowler pointed out to us that the $|2s\rangle$ wavefunction we used in a previous paper [8], while trying various admixtures with the $|2p\rangle$ wavefunction, is not the correct one. Indeed both the wavefunctions there had the same value of η , which is the parameter responsible for their radial extent. On the contrary the correct $|2s\rangle$ state seems to be a very compact one. In this case the $|2s\rangle$ and $|2p\rangle$ radial probability densities are almost the same for $\rho > \sqrt{2}$. (We would like to stress that our experimental data cannot give any information on the wavefunction of the RES for values of ρ smaller than $\sqrt{2}$, which is the distance of the nearest halide shell.)

Hence the conclusion drawn in [8], that the RES of the F center in KI is a pure $|2p\rangle$ like state is incor-

rect ; this is also true for the RES of KBr, which this paper deals with. However the form (4) chosen for the RES remains a good approximation to the correct $|2s\rangle$ state probability density in the region of interest.

In the light of this new evidence the calculation for the matrix element $|x|^2$ seems to remain quite good even if there is some doubt of the correctness of the form (6) of the $|1s\rangle$ state, as pointed recently also by S. Wang *et al.*, *Phys. Rev. B* **7** (1973) 1695. There is

some evidence that the $|1s\rangle$ state actually has a «long tail» that makes the matrix element much bigger than we once thought.

In conclusion we have determined the radial probability density of the RES with great accuracy and in our opinion this should be of considerable value to those who are trying to understand the relaxation process of the F center. However our results do not bear directly on the question of $|2s\rangle$ versus $|2p\rangle$ state !

References

- [1] MOLLENAUER, L. F., PAN, S. and WINNACKER, A., *Phys. Rev. Lett.* **26** (1971) 1643.
- [2] MOLLENAUER, L. F. and PAN, S., *Phys. Rev. B* **6** (1972) 772.
- [3] MOLLENAUER, L. F., PAN, S. and YNGVESSON, S., *Phys. Rev. Lett.* **23** (1969) 683.
- [4] ABRAGAM, A. and BLEANEY, B., *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford) 1970, 228.
- [5] FRÖHLICH, D. and MAHR, H., *Phys. Rev.* **141** (1966) 692.
- [6] HOARE, F. E., JACKSON, L. C. and KURTI, N., *Experimental Cryophysics* (London, Butterworths) 1961, 313.
- [7] HONDA, S. and TOMURA, M., *J. Phys. Soc. Japan* **33** (1972) 1003.
- [8] MOLLENAUER, L. F. and BALDACCHINI, G., *Phys. Rev. Lett.* **29** (1972) 465. In figures 1 and 2 of this work we made a mistake. The number of equivalent nuclei in the halide shells 7 and 13 are 48 and 72 respectively instead of 30 and 56 as stated there. This mistake reflects on the computer simulation, figure 2, in the sense of a better agreement between theory and experiment with a new value for the cross-relaxation constant $\Delta = 10.8$ MHz.
- [9] FOWLER, W. B., *Phys. Rev.* **135** (1964) 1725.
- [10] BOSI, L., PODINI, P. and SPINOLO, G., *Phys. Rev.* **175** (1968) 1133.

DISCUSSION

A. M. STONEHAM. — *a*) Ham's most recent work indicates that the lowest relaxed excited state should be almost entirely s-like, and that any large p-admixture would be inconsistent with other work on the relaxed state ;

b) Ham's analysis of the KCl F-centre suggests that s-p admixture is enough to explain the long lifetime, even without an extended excited state. It would be especially nice to look at this system by your methods.

G. BALDACCHINI. — *a*) I would like to add that

Ham feels that only an s-like wave-function could explain the isotropy of the ESR lines and ENDOR spectra. In any case at moment there is not a complete theoretical work on the nature of the RES.

b) Unfortunately I don't see now how to overcome the experimental difficulties arising from the short lifetime of the F-center in KCl. Even more the *g* factors of the ground state and the RES are not too different from each other and there would be an overlapping of the two EPR lines which is really disturbing in our method.