

Recent developments in magnetic resonance studies of defects in ionic crystals

J. M. Spaeth

Fachbereich Naturwissenschaften I, Experimentalphysik,
Gesamthochschule Paderborn, 4790 Paderborn, W. Germany

Résumé. — Des applications récentes de RPE, RMN et ENDOR sont brièvement passées en revue pour les investigations suivantes : effets de mouvement de défauts ponctuels, influence du changement de phase structurale sur des défauts, autodiffusion, mouvement de dislocation, structure des défauts de basse symétrie, états excités de défauts. La méthode de la révélation des spectres RPE par le comportement des raies d'ENDOR est brièvement décrite pour l'application aux défauts du corps solide. Elle rend possible l'analyse des spectres RPE et ENDOR superposés dus à plusieurs défauts et facilite aussi l'analyse des spectres ENDOR de défauts de basse symétrie.

Abstract. — Recent applications of ESR, NMR and ENDOR to the following investigations are briefly reviewed : motional effects of point defects, influence of structural phase transitions on defects, self diffusion, dislocation motion, structure of low symmetry defects, excited states of defects. The application of ENDOR-induced ESR to solid state defects is briefly described. It allows the analysis of superimposed ESR and ENDOR spectra due to several defects and facilitates also the analysis of ENDOR spectra of low symmetry defects.

1. Introduction. — For many years, magnetic resonance has been a very important tool for the investigation of defects in ionic crystals. In many now well-known cases the atomistic and electronic structure of point defects could finally be established only by the application of magnetic resonance spectroscopy. Also the study of transport phenomena has greatly profited from magnetic resonance investigations.

It is the aim of this paper to draw attention to some more recent developments in the application of Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR) and the combination of both methods, Electron-Nuclear-Double-Resonance (ENDOR). In the last years, these techniques were applied to the study of (i) dynamical properties of defects and transport phenomena, (ii) structure of defects with low symmetry, and (iii) optically excited states of defects. This will briefly be discussed choosing a few illustrative examples. No attempt is made for completeness and it is assumed that the reader is familiar with the basic principles of the magnetic resonance techniques mentioned [1, 2, 3].

2. Dynamical properties of defects and transport phenomena. — Thermally activated motions of defects can be studied with ESR in great detail when a superhyperfine (shf) structure is present. A prominent example for this is the study of the ESR spectra of $H_A(Li^+)$ centres in KCl as a function of temperature by Schoemaker *et al.* [4]. $H_A(Li^+)$ is an interstitial Cl^0 atom stabilized as a Cl_2^- molecule ion in a single negative ion site next to a substitutional Li^+ impurity

ion. The shf lines at low temperature experience a lifetime broadening above 28 K due to a rapid thermally activated motion of the centre. Between 40 and 60 K the spectrum is unrecognizably broadened, but at about 77 K a motionally averaged spectrum emerges with a new shf structure which then again broadens on raising the temperature. At about 90 K all shf structure has disappeared. The analysis of this, which was developed by Schoemaker to a very fine art, has yielded a very detailed picture of two motions occurring with different activation energies. Also other H-type centres show reorientation motions [5].

Dynamical processes occurring at structural phase transitions can also be studied by ESR. Transition metal ions like Fe^{3+} have been used as probes in $SrTiO_4$ first by Müller [6]. The change in the fine structure splitting upon lowering the symmetry from cubic to tetragonal during the structural phase transition was observed. More recently, a similar phase transition was studied in perovskites of the type AMF_3 by Buzaré *et al.* [7], where the shf structure can be observed. An example is $RbCdF_3$ with the defect $Fe^{3+}-O^{2-}$ as a probe. At the phase transition, the $Fe^{3+}-O^{2-}$ bond rotates by an angle of $\pm \varphi$, which is the order parameter of the transition. From the change of the ^{19}F shf structure on going through T_c at 124 K φ is determined to $\pm 0.8^\circ$. In investigations of this kind it seems still necessary to establish that the order parameter of the transition can be determined independently of the paramagnetic defect used as a probe. Possibly ENDOR experiments with different defects will be helpful for this.

A particular useful tool for the study of dynamical effects is the measurement of the nuclear spin lattice relaxation time T_1 in NMR experiments. The lattice contains fluctuating electric field gradients and magnetic fields due to phonons or atomic motions which can interact with the nuclei via magnetic dipole-dipole or electric quadrupole interactions. If in their spectral density the right frequency component is present, they can induce transitions between the nuclear Zeeman levels.

In the simple case, where the time fluctuations can be characterized by a single correlation time τ_c , one has approximately [2]

$$\frac{1}{T_1^{(j)}} \simeq \langle \omega_j^2 \rangle \frac{\tau_c}{1 + \omega_j^2 \tau_c^2}$$

where $\langle \omega_j^2 \rangle$ is the average interaction energy between the nuclear spins. The time range which can be measured is determined by ω . $T_1 = T_{1Z}$, the Zeeman relaxation time for $\omega = \omega_0 = \gamma_1 B_0$. For atomic diffusion studies it is desirable to measure longer times τ_c . This is possible with spin locking experiments where T_1 is measured as $T_{1\rho}$ in the rotating frame, where $\omega = \omega_1 = \gamma_1 B_1 \ll \omega_0$ [2]. Using very sophisticated pulse sequence experiments B_1 can be effectively brought to zero, so that $\omega = \omega_{\text{local}} \ll \omega_1$ where ω_{local} is only determined by the local spin-spin interactions. In these experiments very slow motions can be measured. In figure 1 the available time range for τ_c is sketched [8].

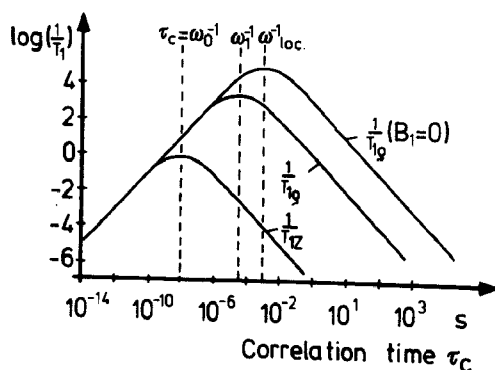


Fig. 1. — Range of correlation times which can be determined by measuring T_{1Z} , $T_{1\rho}$, and $T_{1\rho}(B_1 = 0)$. After [8].

The thermally activated motion of off-centre Ag^+ ions in RbCl could be measured by Kanert *et al.* [9] as a function of temperature. The fluctuating electric dipole moments of the off-centre Ag^+ ions caused an additional relaxation rate at the ^{87}Rb nuclei with a maximum at about 10–12 K.

An important application of relaxation time measurements is the investigation of transport phenomena such as self-diffusion. A comprehensive study was performed in the fluorites CaF_2 , SrF_2 and BaF_2 , both pure and doped with paramagnetic impurities, by Strange *et al.* [10, 11], over a wide range of corre-

lation times measuring T_{1Z} , T_2 , $T_{1\rho}$ and $T_{1\rho}(B_1 = 0)$. In BaF_2 11 orders of magnitude were covered. The interpretation of the relaxation rates is usually not easy. The main theoretical problem is the precise calculation of the spectral density function of the fluctuations in terms of a mean residence time τ_c of an atom on a lattice site. When self-diffusion is sufficiently fast, spin locking experiments with the sample in a strong magnetic field gradient can be performed (PFG method) and the diffusion constant can thus be measured directly [12]. The first experimental realization of this at high temperature by Gordon *et al.* [13] gave for fluorites very good agreement with data obtained by conductivity measurements [11] and the interpretation of the relaxation data assuming a monovacancy mechanism for self-diffusion.

Another very interesting development is the observation of dislocation motion in alkali halides with NMR. It could be shown by Hut *et al.* and Hackelöer *et al.* [14, 15] using the Jeener sequence [16] to measure very slow $T_{1\rho}(B_1 = 0)$ relaxation times that an additional relaxation rate is induced during plastic deformation by the motion of dislocations. In the presence of a strain rate $\dot{\epsilon}$ the spin-echo signal decays faster than for $\dot{\epsilon} = 0$. The analysis yielded valuable information about the mechanism of dislocation motion [16].

Localized motions of atoms can also be studied by ENDOR. In the case of hydrogen atoms which occupy cation vacancy sites in KCl and RbCl , there is a large effect of the local mode vibration on the ENDOR spectrum. The ENDOR lines shift by about 200 kHz to higher frequencies within a 60 K temperature increase [17]. Because of the high precision of the ENDOR, also motions of heavier atoms with smaller vibrational amplitudes should be observable.

3. Structure of defects with low symmetry. — The best method to determine the atomistic and electronic structure of a paramagnetic defect is ENDOR, since it allows to resolve the superhyperfine and quadrupole interactions with many shells of neighbouring nuclei. Recently, an improvement of the experimental arrangement could be achieved by the availability of low noise microwave amplifiers. This enables one to work with a homodyne system with about the same sensitivity at low modulation frequencies, which are usually necessary, as one would achieve with the superheterodyne systems so far [18]. Another experimental improvement is achieved by hooking the ENDOR spectrometer fully on line with a computer. This allows fully automatized measurements and makes for instance the measurement of angular dependencies in steps of single degrees for various crystal planes feasible, what to do *by hand* would be very tedious. Such measurements are necessary to analyse complicated spectra which occur especially for low symmetry defects. Further advantages are

the possibility of digital filtering of the spectra, automatic peak searching and applying least square fits when diagonalizing the Spin Hamiltonian to determine the interaction parameters.

The analysis of ENDOR spectra can get rather problematic when several ESR spectra are superimposed, a fact often happening in radiation damage studies. If the ENDOR lines of different defects lie within the same frequency range, then the analysis is usually very difficult, if not impossible. To overcome this, the technique of ENDOR-induced ESR measurements has proved to be very useful. This technique was first applied by Hyde [19] and a few times later to organic molecules [20, 21]. In an ENDOR experiment the magnetic field is kept constant and the rf-emitter is swept until the double resonance condition is fulfilled. In ENDOR-induced ESR one fixes the rf-emitter at a particular ENDOR transition and sweeps the magnetic field, whereby one monitors the change of the ENDOR line. One observes an image of that ESR spectrum which is responsible for the particular ENDOR line and thus the ESR of different defects can be separated and the ENDOR line can be assigned to its defect. During the field sweep the ENDOR frequency shifts which can be accounted for by automatic tuning of the emitter. If the crystal contains only nuclei with $I = 1/2$, then the true ESR spectrum is obtained irrespective of which ENDOR line is used. If quadrupole interactions are present, then the number of lines and the linewidth of the ENDOR-induced ESR spectrum depends on the ENDOR transition used. An example is given in figure 2 for the two F centres in BaFCl [22]. If for instance a Ba-ENDOR line of the $F(\text{Cl}^-)$ centre is used, not the full ESR spectrum of the $F(\text{Cl}^-)$ centre is reproduced. The measurement with other ENDOR lines with smaller interactions yields the full ESR spectra and separates the two defects. For the case of several equivalent nuclei which are split by second order superhyperfine structure, further complications occur. ENDOR-induced ESR measurements can be used to determine the g factors of superimposed ESR spectra. They also allow the assignment of ENDOR lines to particular nuclei in low symmetry defects, to determine the sign of interaction constants, and to measure quadrupole interactions which are not resolved in the ENDOR spectrum. It was also possible to establish in the non-stoichiometric material β -alumina, that the large width of the ENDOR lines is due to a spread in superhyperfine interactions. A detailed account of the application of the ENDOR-induced ESR method for the study of defects in solids will be given elsewhere (J. R. Niklas and J. M. Spaeth, to be published).

4. Optically excited states of defects. — The technique of optically detecting the magnetic resonance (ODMR) of excited states is now well established [23]. There are mainly two approaches. One is the obser-

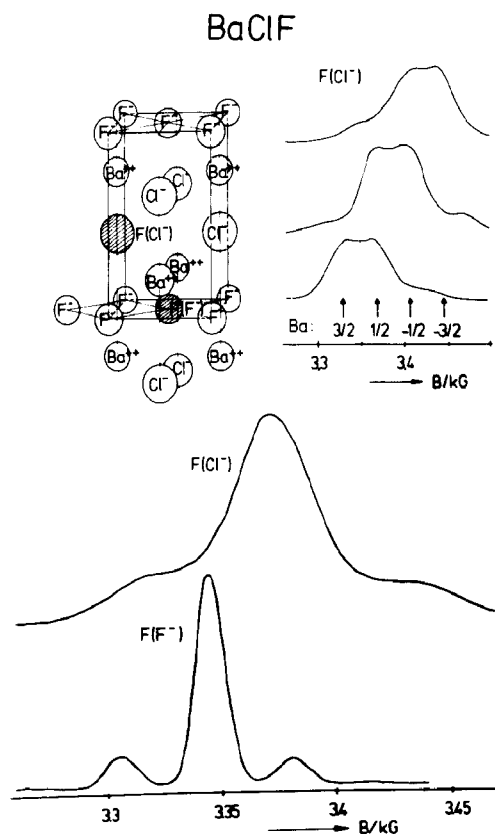


Fig. 2. — ENDOR-induced ESR for F centres in BaFCl. Upper half of figure: crystal structure with $F(\text{Cl}^-)$ and $F(\text{F}^-)$ centres (left); ENDOR-induced ESR for the 3 Ba-quadrupole-ENDOR lines. Lower half of figure: ENDOR-induced ESR for ^{19}F -ENDOR lines of $F(\text{Cl}^-)$ and $F(\text{F}^-)$ centres.

vation of the magnetic circular dichroism of the absorption, which relies on spin polarization memory within the optical pumping cycle, which was especially used for the study of F centres in alkali halides where the circular polarization of the fluorescence light is very small [24, 25]. From recent experiments it seems that there is evidence for more than one relaxed excited state of the F centre [26]. Very recently, however, Imanaka *et al.* could observe the F centre resonance via magnetic circular polarization of the emission [27]. This is the more general technique. So far it was mainly used to study electronic triplet states such as F centres in CaO and MgO [28]. It was demonstrated recently by Merle d'Aubigné *et al.* [29] that the ESR of F centres in CaO is broadened by strain and spin orbit coupling. By selecting low and high frequency parts of the zero-phonon line when detecting the magnetic resonance, a shift and narrowing of the EPR line was observed, since F centres with a particular strain distribution were selected this way. Also using selective optical pumping states with a definite internal stress could be detected [30].

Recently, it was possible to resolve a shf structure with Mg^{++} in $F_A(\text{Mg})$ centres in CaO in spite of the low abundance of about 10 % of magnetic ^{25}Mg [31].

A shf structure with the centre nuclei was resolved for the self-trapped exciton (STE) in various alkali halides [32-35] and alkaline earth fluorides [36]. There is also very interesting work on the STE in the silver halides [37-39]. The different ESR spectra for the relaxed excited states in AgCl presented by the 3 groups working on this differ all from each other and it seems that the dependence of the spectra on purity of the samples, way of excitation (X-ray or optical excitation) and modulation frequency is not yet fully understood.

Very few ENDOR experiments have been performed for excited states using optical detection. There is the work on F centres in alkali halides [40, 41]

using the spin memory technique and the work by Jaccard *et al.* [42] for close pairs of F centres which relies ultimately on the concentration dependence of the quantum yield for the luminescence and is restricted to F centres in alkali halides. More recently Block *et al.* [43] performed ENDOR experiments on the STE in KCl and could resolve the interaction with the central and further nuclei. Rather surprisingly, two different quadrupole interaction parameters for the two central Cl nuclei were observed. The discussion about the explanation of this result is still going on. There may be two different relaxation configurations [43] or an off-centre configuration [44]. Further experiments would be desirable.

References

- [1] SLICHTER, C. P., *Principles of Magnetic Resonance* (Harper and Row, N.Y.) 1963.
- [2] ABRAGAM, A., *The Principles of Nuclear Magnetism*, Oxford, 1961.
- [3] KEVAN, L. and KISPert, L. D., *Electron Spin Double Resonance Spectroscopy* (John Wiley and Sons, N.Y.) 1976.
- [4] SCHOEMAKER, D. and YASAITIS, E. L., *Phys. Rev. B* **5** (1972) 4970.
- [5] SCHOEMAKER, D., *J. Physique Colloq.* **37** (1976) C7-63.
- [6] MÜLLER, K. A., *Helvetica Physica Acta* **31** (1958) 173.
- [7] BUZARÉ, J. Y. and FAYET, J. C., *Solid State Commun.* **21** (1977) 1097.
- [8] KANERT, O., private communication.
- [9] KANERT, O. and MALI, M., *Phys. Lett.* **69A** (1979) 344.
- [10] FIGUEROA, D. R., CHADWICK, A. V. and STRANGE, J. H., *J. Phys. C: Solid St. Phys.* **11** (1978) 55.
- [11] GORDON, R. E. and STRANGE, J. H., *J. Chem. Soc.* (1979), in press.
- [12] STEJSKAL, E. O. and TANNER, J. E., *J. Phys. Chem.* **42** (1965) 288.
- [13] GORDON, R. E. and STRANGE, J. H., *J. Phys. C: Solid St. Phys.* **11** (1978) 3213.
- [14] HUT, G., SLEESWYK, A. W., HACKELÖER, H. J., SELBACH, H. and KANERT, O., *Phys. Rev. B* **14** (1976) 921.
- [15] HACKELÖER, H. J., SELBACH, H., KANERT, O., SLEESWYK, A. W. and HUT, G., *Phys. Status Solidi (b)* **80** (1977) 235.
- [16] JEENER, J. and BROEKAERT, P., *Phys. Rev.* **157** (1967) 232.
- [17] HOENTZSCH, Ch. and SPAETH, J. M., *Phys. Status Solidi (b)* **88** (1978) 581.
- [18] HOENTZSCH, Ch., NIKLAS, J. R. and SPAETH, J. M., *Rev. Sci. Instrum.* **49** (1978) 1100.
- [19] HYDE, J. S., *J. Chem. Phys.* **43** (1965) 1806.
- [20] ATHERTON, N. M. and BLACKHURST, A. J., *J. Chem. Soc. Faraday Trans. II* **68** (1972) 470.
- [21] ROBINSON, B. H., DALTON, A., BETH, A. H. and DALTON, L. R., *Chem. Phys.* **18** (1976) 321.
- [22] NIKLAS, J. R., HEDER, G., YUSTE, M. and SPAETH, J. M., *Solid State Commun.* **26** (1978) 169.
- [23] GESCHWIND, S., in *Electron Paramagnetic Resonance*, ed. by S. Geschwind (Plenum N.Y.) 1972.
- [24] MOLLENAUER, L. F., PLAN, S. and INGVerson, S., *Phys. Rev. Lett.* **23** (1969) 683.
- [25] WINNACKER, A., MAUSER, K. E. and NIESERT, B., *Z. Phys.* **B 26** (1977) 97 and 107.
- [26] HAHN, K., REYHER, H. J., VETTER, Th. and WINNACKER, A., *Phys. Lett.* **27A** (1979) 363.
- [27] IMANAKA, K., WADA, I., TANAKA, M. and OHKURA, H., *J. Phys. Soc. Japan* **45** (1978) 2041.
- [28] HENDERSON, B. and O'CONNELL, D. C., *Semiconductors and Insulators* **3** (1978) 299.
- [29] DANG, L. S., MERLE D'AUBIGNÉ, Y. and ROMESTAIN, R., *Semiconductors and Insulators* **3** (1978) 151.
- [30] BONTEMPS-MOREAU, N., BOCCARA, A. C. and THIBAUT, P., *Semiconductors and Insulators* **3** (1978) 165.
- [31] DAWSON, P., McDONAGH, C. M., HENDERSON, B. and WELCH, L. S., *J. Phys. C: Solid St. Phys.* **11** (1978) L-983.
- [32] MARRONE, M. J., PATTEN, F. W. and KABLER, M. N., *Phys. Rev. Lett.* **31** (1973) 467.
- [33] WASIELA, A., ASCARELLI, G. and MERLE D'AUBIGNÉ, Y., *Phys. Rev. Lett.* **31** (1973) 993.
- [34] CALL, P. J., HAYES, W., HUZIMURA, R. and KABLER, M. N., *J. Phys. C: Solid St. Phys.* **8** (1975) L-56.
- [35] HAYES, W. and OWEN, I. B., *J. Phys. C: Solid St. Phys.* **10** (1977) L-197.
- [36] CALL, P. J., HAYES, W. and KABLER, M. N., *J. Phys. C: Solid St. Phys.* **8** (1975) L-60.
- [37] MURAYAMA, K., MORIGAKI, K., SAKURAGI, S. and KANZAKI, H., *J. Phys. Soc. Japan* **41** (1976) 1617.
- [38] HAYES, W., OWEN, I. B. and WALKER, P. J., *J. Phys. C: Solid St. Phys.* **10** (1977) 1751.
- [39] MARCHETTI, A. P., EACHUS, R. S. and TINTI, D. S., *Phys. Lett.* **65A** (1978) 363.
- [40] MOLLENAUER, L. F. and PAN, S., *Phys. Rev. B* **6** (1972) 772.
- [41] MOLLENAUER, L. F. and BALDACCHINI, G., *Phys. Rev. Lett.* **29** (1972) 465.
- [42] JACCARD, C. and ECABERT, M., *Semiconductors and Insulators* **3** (1978) 195.
- [43] BLOCK, D., WASIELA, A. and MERLE D'AUBIGNÉ, Y., *J. Phys. C: Solid St. Phys.* **11** (1978) 4201.
- [44] SONG, K. S. and LEUNG, C. H., *J. Phys. C: Solid St. Phys.* **12** (1979) L-67.