Pulsed nuclear-nuclear double resonance

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Nuclear–nuclear double resonance spectra are investigated. A structural classification is presented for the defects and correspondingly for the spectra in crystal with space group O_h^5. The orientational dependence of the Hamiltonian is obtained for the possible defect positions in the laboratory coordinate frame. The nuclear-nuclear double resonance experiment was performed on an NaF:Li crystal. Saturation of the sparse nuclei was effected by sinusoidal modulation of the amplitude of the RF field, a method more effective than (or comparable with) saturation by periodic 180° modulation of the phase. The nuclear-nuclear double resonance method is used to measure the impurity concentration. The constants of the Hamiltonian are determined.

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A large proportion of all the possible crystal-lattice distortions is made up of diamagnetic defects, such as impurity atoms, vacancies, etc. A method that offers great possibilities for the investigation of diamagnetic defects is the nuclear-nuclear double resonance (NNDR) method. Its sensitivity exceeds by several orders that of detecting NMR signals,[1–3] so that it becomes possible to investigate small defect concentrations as well as to study the nature, structure position, and concentration of the defects and a number of other parameters.[4–7]

The present paper is devoted to a study of the NNDR spectra of an NaF crystal containing a minute amount of impurities. The entry of the impurity atom causes in the general case a change in the local symmetry of the ligands, namely, lowering of the cubic symmetry of the surrounding nuclei. This produces a nonzero static electric-field gradient at the ligand positions and a quadrupole splitting of the NMR line at the corresponding nuclei. The transition frequencies shifted by the quadrupole interactions beyond the limits of the fundamental NMR line of Na could be observed separately and were the subject of the investigation.

Before we describe the experimental results, we present a classification of the defects and their spectra[8] which are possible in structures with space group O_h^5 to which the investigated NaF crystal belongs (see Table I). The position symmetry groups, obtained when a defect is produced in a structure, belong one of the subgroups G_α of the point group of the crystal (column 1). In column 2 are listed the orientations of the symmetry elements, and the following notation is used: +—axis of [100] type, (+)—axis of [110] type, and the symbol ○ marks a twofold axis. Column 3 indicates the types of positions: K_M—number of magnetically nonequivalent positions (spectra) in the overall orientation of the magnetic field relative to the crystal: G_L—Laue-symmetry of the position, which determines the expected type of symmetry of the Hamiltonian (i.e., of the angular dependence of the spectrum); G_β—intersection of the groups O_h and ∞/mm, which occurs when the magnetic field is oriented along the indicated directions. The rows of the table give the scheme of superposition of the magnetically conjugate spectra for the nuclei occupying the positions G_α. To abbreviate the notation, the number of spectra of identical multiplicity is indicated in the form of a product (e.g., 2 · 6 means six spectra of multiplicity 2). It is immaterial for the superposition scheme whether the lowering of the symmetry is due, for example, to displacement of the impurity, the displacement of the environment, or both. All that matters is which symmetry group describes the position in which the observation is carried out.

The use of the table can be illustrated with a rhombically distorted position (C_{2v}) as an example. If $\mathbf{H}_0 \parallel [110]$, three different spectra should be observed in the experiment: two single and one with multiplicity 4. Next, if the field is parallel to the (100) plane, then four spectra should be observed, two single and two with twofold superposition. The use of the table makes it possible, if all the spectra are registered, to determine the symmetry of a position without investigating the orientational dependence, and to avoid errors in the interpretation of the results.

The NNDR experiment was performed in the following manner: The temperature of the dipole-dipole pool (DDP) was lowered by two phase-shifted RF pulses acting at the resonant frequency 21.200 MHz of the F nuclei (I nuclei). The distinguishing features of the cooling of the DDP were considered in[9,10]. Saturation of the investigated nuclei (S nuclei) was with the aid of sinu-

TABLE I. Superposition of magnetically conjugate spectra in structures with space group O_h^5 (CaF_2, NaF).

G_α	Axes	Position	K_M	G_L	$H \parallel [111]$ $G_\beta : D_{3d}$	[100] D_{4h}	[110] D_{2h}	(110) C_{2h}	(100) C_{2h}
C_{3v}	(+)3– +++	f	4	D_{3d}	1+3	4	2+2	1+1+2	2+2
C_{4v}	(++)+	e	3	D_{4h}	3	1+2	1+2	1+2	1+1+1
D_{2h}	(++)+	d	6	D_{2h}	3+3	2+4	1+1+4	1·2+2·2	1·2+2·2
C_{2v}	(○+)+	(h, i)	6	D_{2h}	3+3	2+4	1+1+4	1·2+2·2	1·2+2·2
C_{2v}	(++)○	g	6	D_{2h}	3+3	2+4	1+1+4	1·2+2·2	1·2+2·2
C_s	+– –	j	12	C_{2h}	6+6	4+4+4	2·2+4·2	2·6	1·4+2·4
C_s	(+)– –	k	12	C_{2h}	3·2+6	4+8	2·2+4·2	1·2+2·5	2·6
C_1	– – –	l	24	C_i	6·4	8·3	4·6	2·12	2·12

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soidal modulation of the RF field amplitude.[11,12] This modulation is equivalent to simultaneous action of three RF fields at the frequencies ω_0 and $\omega_0 \pm \Omega$, which can be written in the form

$$W=2\omega_{1S}\cos\omega_0 t+m\omega_{1S}\cos(\omega_0-\Omega)t + m\omega_{1S}\cos(\omega_0+\Omega)t, \tag{1}$$

where m is the modulation parameter. The rate of change of the DDP temperature is determined by Provotorov's equations.[13,14] If the spectrum of the saturating pulse is symmetrical relative to $\omega_0=\gamma_S H_0$, then the Zeeman and dipole energies vary independently and the rate of change of the DDP temperature with the S nuclei saturated is given by

$$1/T_S=\pi(\omega_{1S}\Omega)^2 g^S(\Omega)/8L(\gamma_I{}^I H_L)^2, \tag{2}$$

where

$$L=\gamma_I{}^2 N_I I(I+1)/\gamma_S{}^2 N_S S(S+1).$$

Formula (2) is similar to the expression for not-strictly resonant saturation of an NMR line,[13–15] but a factor $1/L$ appears in the case of saturation on the wing of the line of the sparse nuclei. Comparison with the analogous expression for the method with 180° phase reversal gives for the ratio of the saturation rates

$$T_{\rm ph}/T_S=\pi\Omega^2 g^S(\Omega)\tau H_{1S}{}^2/16H_{\rm ph}^2. \tag{3}$$

Here $1/T_{\rm ph}$ is the rate of change of the DDP temperature for saturation by 180° phase modulation; $H_{1S}=2\omega_{1S}/\gamma_S$ and $H_{1\rm ph}$ are the amplitudes of the saturating fields. For estimating purposes we can put $g^S(\Omega')=g^S(0)/2$ and $g^S(0)=1/2\Omega'$ (Ω' corresponds to the maximum rate of change of the DDP temperature), and then

$$T_{\rm ph}/T_S=\pi\Omega'\tau H_{1S}{}^2/64H_{\rm ph}^2. \tag{4}$$

At $\Omega'=10$ kHz, $\tau=5$ msec, and equal RF fields, $H_{1S}=H_{1\rm ph}$, the last expression yields $T_{\rm ph}/T_S=2.5$, which agrees with the experimental value ≈ 2.2. Thus, saturation by sinusoidal modulation is more effective than the phase reversal method (or is at least comparable with it). The sinusoidal modulation makes it possible to investigate the line shape of the sparse nuclei[12] and is easier to effect in experiment. The DDP temperature is monitored with a third RF pulse; the change of the pool temperature by the saturating pulse was registered as the NNDR signal.

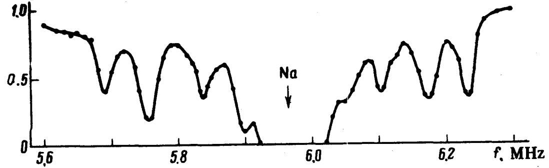

FIG. 1. NNDR spectrum in NaF : Li. Magnetic field $\mathbf{H}_0 \parallel [110]$, saturating-pulse duration ≈ 1 sec with sinusoidal modulation of the RF field amplitude ($H_{1S} \approx 5$ G) at a frequency $\Omega = 10$ kHz. Temperature 77 K.

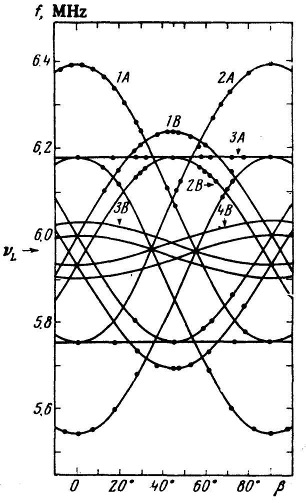

FIG. 2. Orientational dependence of the quadrupole splittings of the NMR line of Na in tetragonally and rhombically distorted positions for crystal rotation around the [010] axis.

In the investigated NaF crystal we observed by the NNDR method the quadrupole spectra of Na. As shown by subsequent investigation, the appearance of these spectra is due to the presence in the sample of the Li ions, which were also observed by the double-resonance method.

An analysis of the orientational dependence has revealed two types of distorted positions of Na, namely C_{4v} and C_{2v}. The existence of such positions indicates that the impurity substitutes for Na ions. A typical spectrum is shown in Fig. 1. The large dip at the center belongs to the unperturbed Na nuclei in the crystal. The NNDR pulse sequence was repeated every 20 seconds, corresponding to saturation of the F nuclei ($T_{1Z}^{\rm F} \approx 25$ sec at 77 K). The use of this regime greatly reduced the time of the experiment at the expense of a negligible loss of sensitivity. The orientational dependence of the quadrupole splittings for rotation of the crystal about the [010] axis is shown in Fig. 2.

The theoretical angular dependence of the possible spectra (see the table) can be obtained by using the form of the quadrupole Hamiltonian corresponding to the position G_α. For the low-symmetry position C_1 in the l. s., this Hamiltonian contains all the terms[16]:

$$\hat{\mathscr{H}}=-\gamma\hbar I_Z H_0+B_2^0 O_2^0+B_2^1 O_2^1+\tilde{B}_2^1\tilde{O}_2^1 + B_2^2 O_2^2+\widetilde{B_2^2}\widetilde{O}_2^2, \tag{5}$$

here

$$B_2^0=e^2 Q q_{ZZ}/4I(2I-1)=\nu_Q h/6=Aq_{ZZ},$$

$$B_2^1=4Aq_{XX},\quad \tilde{B}_2^1=-4Aq_{YZ},\quad B_2^2=A(q_{XX}-q_{YY}),\quad \tilde{B}_2^2=-2Aq_{XY},$$

where $q_{X_iX_j}=e^{-1}\partial^2 V/\partial X_i\partial X_j$ and V is the potential of the electric field. We represent the rotation that determines the orientation of the magnetic field relative to the principal axes of the local crystal field in the form of two successive rotations of the crystal. In the initial state the Z' axis of the crystal field is parallel to $\mathbf{H}_0$ and $Y' \parallel Y$ (see Fig. 3). The first rotation is through an angle β that specifies the position of the magnetic field relative to the l. s. (X, Y, Z), which is rigidly fixed in the crystal. The second rotation is through the Euler

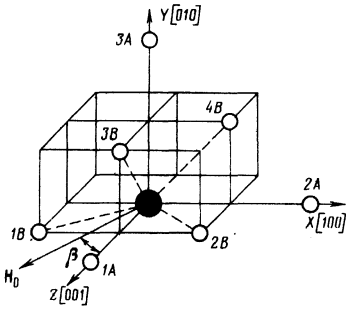

FIG. 3. Arrangement of the tetragonally and rhombically distorted positions of Na around the Li impurity ion.

angles α_i, β_i, and γ_i. We assume that all the angles are reckoned from the l. s. and their sequence is: first γ_i, then β_i and α_i.[17] These angles determine the orientation of the principal axes of the crystal field relative to the l. s. The transformation of O_2^m and $\tilde{O}_2^m$ in the Hamiltonian can be obtained by expressing them in terms of irreducible tensor operators whose transformation is determined by Wigner coefficients.[17] The formulas for the transformation of O_2^m and $\tilde{O}_2^m$ for the rotations indicated above are too complicated to be presented here.

As a result of these transformation, the Hamiltonian (5) can be expressed in the form

$$\mathscr{H}=-\gamma\hbar I_zH_0+f_0O_2{}^0+f_1O_2{}^1+\tilde{f}_1\tilde{O}_2{}^1+f_2O_2{}^2+\tilde{f}_2\tilde{O}_2{}^2. \tag{6}$$

The quantity f_m is obtained by summing the coefficients of O_2^m. The result is a formula that is convenient for the analysis of the experimental results up to second-order perturbation theory inclusive:

$$\begin{aligned}\nu_{m-1,m}=\nu_L+f_0(3-6m)+\frac{(f_1{}^2-\tilde{f}_1{}^2)}{8\nu_L}[24m(m-1)-a+9]\\+\frac{(f_2{}^2-\tilde{f}_2{}^2)}{4\nu_L}[-12m(m-1)-a-6],\end{aligned} \tag{7}$$

where

$$\nu_L=\gamma H_0/2\pi,\ a=4I(I+1).$$

We shall use the foregoing results to analyze the experimentally observed quadrupole spectra of tetragonal (C_{4v}) and rhombic (C_{2v}) symmetry. The corresponding Hamiltonians, in terms of the principal axes, are[16]

$$\begin{aligned}\mathscr{H}_T&=-\gamma\hbar I_zH_0+{}^TB_2{}^0O_2{}^0,\\ \mathscr{H}_P&=-\gamma\hbar I_zH_0+{}^PB_2{}^0O_2{}^0+{}^PB_2{}^2O_2{}^2.\end{aligned} \tag{8}$$

By simple calculations we obtain for arbitrary spin S, in first-order perturbation theory, the following formulas for the orientational dependence of the quadrupole splitting of magnetically conjugate spectra:

Tetragonal positions:

1A. $(\alpha_i=0,\quad \beta_i=0,\quad \gamma_i=0)$,
$\Delta=bB_2{}^0(1+3\cos 2\beta)$,

2A. $(\alpha_i=0,\quad \beta_i=90°,\quad \gamma_i=0)$,
$\Delta=bB_2{}^0(1-3\cos 2\beta)$,

3A. $(\alpha_i=90°,\quad \beta_i=90°,\quad \gamma_i=0)$,
$\Delta=-2bB_2{}^0$.

Rhombic positions

1B. $(\alpha_i=0,\quad \beta_i=-45°,\quad \gamma_i=0)$,
$\Delta=b[d+c\sin 2\beta]$,
2B. $(\alpha_i=0,\quad \beta_i=+45°,\quad \gamma_i=90°)$,
$\Delta=b[d-c\sin 2\beta]$,
3B. $(\alpha_i=90°,\quad \beta_i=+45°,\quad \gamma_i=90°)$,
$\Delta={}^1/_2bd(3\cos 2\beta-1)$,
4B. $(\alpha_i=45°,\quad \beta_i=90°,\quad \gamma_i=0)$,
$\Delta={}^1/_2bd(3\cos 2\beta+1)$.

Here

$$\Delta=\nu_{m-1,\,m}-\nu_L,\quad b=(3-6m)/4h,$$
$$d=B_2{}^0-B_2{}^2,\quad c=3B_2{}^0+B_2{}^2.$$

We note that the multiplicity of the superposition of all the spectra is equal to unity, with the exception of the spectra of positions $3B$ and $4B$, whose multiplicity is equal to two.

The indicated values of the angles α_i, β_i, and γ_i for the tetragonal positions correspond to axes directed along the edges of a cube. For the rhombic positions, the Z' axis is directed along the line joining the impurity and the registered nucleus, and the X' axis has a direction of the [100] type. The frequency difference of the transitions $3/2\leftrightarrow-1/2$ for position $1B$ and $3/2\leftrightarrow 1/2$ for the position $2B$ is independent of the orientation and yields an expression for B_2^2.[7]

An analysis of the experimental results yields the following values for the parameters of the Hamiltonians:

Tetragonal position:

$${}^TB_2{}^0/h=e^2q_{zz}Q/12h=71.5\pm0.5\text{ kHz}$$

Rhombic position

$${}^PB_2{}^0/h=45.4\pm0.5\text{ kHz}\quad {}^PB_2{}^2/h=24.4\pm2\text{ kHz}$$

(the asymmetry parameter is $\eta=B_2^2/B_0^2=0.54\pm0.06$).

The obtained constants of the Hamiltonian are very close to those given in [1], where the NNDR method was used to investigate an NaF : Li crystal containing 0.25% Li relative to the number of fluorine atoms. The present experiment differs in that the I nuclei were the F (rather than Na) nuclei, and the Li concentration investigated was smaller by a factor of four. In addition, in our case we registered simultaneously the ^{7}Li nuclei and the Na nuclei in distorted positions. A comparison of the amplitudes of this signal has made it possible to state in addition that the onset of noncubic positions in the investigated NaF crystal is due to the presence of Li nuclei.

Measurement of the concentration by the NNDR method was carried out in the following manner: The change of the dipole-system signal after the third pulse, in the case of saturation by fast modulation of the phase ($dH_{1\text{ph}}/dt\gg H_{1\text{ph}}^2$) with a switching period τ much larger than the time T_{IS} of the cross relaxation between the DDP and the Zeeman system of the S nuclei in the rotating coordinate system) is described by the formula[4]

$$S_d(n\tau)/S_d(0)=e^{-2n\varepsilon}.$$

By varying the number n we determined the experimental value

$$\varepsilon = H_{\mathrm{ph}}^2 / L\,{}^{I} H_L^2. \quad (9)$$

From (9) we obtained the ratio N_S/N_I of the nuclei. The satisfaction of the condition $\tau \gg T_{IS}$ was monitored against the ratio $\varepsilon/H^3_{1\mathrm{ph}}$, which should be independent of τ and $H_{1\mathrm{ph}}$ if this inequality holds. The experimental value of this quantity for Na nuclei in tetragonally distorted positions (transition $f = 6.175$ MHz at $\mathbf{H}_0 \parallel [100]$) is equal to $(74 \pm 10) \times 10^{-6}$ G^{-2}. The ratio of the number of Na nuclei in the tetragonally distorted positions to the number of F nuclei in the sample is therefore ~0.6%, or (0.1 ± 0.02)% when converted to the number of the added impurities. The concentration of ^{7}Li in the sample was measured at $\mathbf{H}_0 \parallel [110]$, $\tau = 10.4$ msec, and $H_{1\mathrm{ph}} = 2.7$ G. The value of $\varepsilon/H^2_{1\mathrm{ph}}$ was found to be $(168 \pm 20) \times 10^{-6}$ G^{-2}. Consequently the ratio of the number of ^{7}Li atoms to the number of F atoms is (0.062 ± 0.008)%, in agreement with the reported measurement results.

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Radiation polarization and ferromagnetic ordering in a semiconductor laser

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By pumping the electrons and holes in a semiconductor by an external source it is possible to establish a quasi-Fermi distribution of the nonequilibrium carriers. At temperatures below a certain critical value T_g this produces a simultaneous Bose condensation of electron-hole pairs and photons, meaning the onset of a lasing regime in the system. If the electron and hole densities are unequal (because of doping), singlet and triplet electron-hole pairings can coexist at $T \leq T_C (T_C \leq T_g)$, thus attesting to the appearance of ferromagnetic ordering. Spin-orbit interaction of the electrons with the radiation, by causing spin flip of the electrons in interband transitions, produces at $T \leq T_C$ in the laser radiation a circular polarization proportional to the degree of the ferromagnetic order.

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1. It is known that metals with congruent sections of the Fermi surface are unstable to electron-hole pairing (exciton instability[1]) and are subject also to phonon instability.[2] Consequently, either electron and ion charge-density waves (CDW) or an electron spin density wave (SDW) is produced in the stable state.

A similar situation can obtain in semiconductors under nonequilibrium conditions, when the external source produces an excess of electron density in the conduction band or of hole density in the valence band. If the energy relaxation time τ_E within each band is much shorter than the interband recombination time τ_R, then the electron and hole distribution functions are of quasi-Fermi form. At sufficiently high pump intensity, the Fermi quasi-levels μ_e of the electrons and μ_h of the holes are located respectively inside the conduction and valence bands, i.e., population inversion takes place. A situation is then possible wherein the constant-energy surfaces correspond to the Fermi quasi-levels of the electrons and holes are almost congruent.

In this case, exciton instability can take place and charge- or spin-density waves can be produced if the

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