The system SF_6 - CO_2

Critical phase				SF_6 added,	Change in pressure,
$N_2 \times 10^3$	p_{cr}, kg/cm^2	T, °C	Weight of phase, g	g	$kg/cm^2 \times 10^2$
10.70	38.708	45.180	12.2749	0.8713	-2.7
10.00	38.699*	45.223*	12.2733	0.2875	-1.2
9.76	38.680	45.218	12.2300	0.9895	-2.4

* $p = p_{cr} + 0.015$ kg/cm^2, $T = T_{cr} + 0.013$°C.
Total volume of system 16.670 cm^3.

also calculated from the data given in [3].

We see thus that it is necessary to excercise great caution in extrapolating the ordinary thermodynamic relations for solutions into the region of the critical point. It can apparently also be regarded as firmly established that $(\partial p/\partial N_2)_{T,v}$ is finite and $(\partial p/\partial v)_{T,N_2}$ is proportional along the critical curve of the solution to the impurity concentration (Eq. (3)), at least to concentrations ~0.1%.

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* By definition, $(\partial V/\partial n_1)_{p,T,n_2} = v_1$ (we are considering a binary solution), where V is the total volume of the solution, p the pressure, T the temperature, n the number of moles, 1 the solvent, and 2 the solute. See [1] concerning the partial molar quantities.

ELECTRON NUCLEAR DOUBLE RESONANCE OF F CENTERS IN KCl (REMOTE COORDINATION SPHERES)

S. S. Ishchenko, N. P. Baran, M. F. Deigen, and M. A. Ruban
Institute of Semiconductors, Ukrainian Academy of Sciences

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The electron-nuclear double resonance method (ENDOR) permits the study of the hyperfine interaction of impurity centers in a crystal with a large number of lattice nuclei. This makes it possible to determine a number of properties of such centers and to clarify their nature, their topography, and the spatial distribution of the electron-cloud density. The larger the number of lattice nuclei that can be taken into consideration, the more complete the information.

Particularly important are results of measurement of the hyperfine interaction with remote nuclei, since this makes it possible to study the asymptotic form of the wave function of the localized electron. The latter is important, in particular, for a determination of the structure of the conduction band and of the effective-mass tensor [1].

The most thorough ENDOR study was made of the hyperfine interaction of the F centers in alkali-halide crystals (cf., e.g., [2,3]). In such investigations they usually recorded signals from nuclei in not more than eight coordination spheres.

In [4,5] they succeeded in exceeding this limit and measuring the hyperfine interaction of the F-center electron with nuclei up to the sixteenth coordination sphere.

We present in this communication the results of an investigation of the hyperfine interaction of F centers in KCl with the nuclei of the coordination spheres XXV ([500]) and XLIX ([700]).

We used KCl single crystals with F-center density 10^{18} cm^{-3} for the measurements.

The measurements were made with an ENDOR superheterodyne spectrometer operating in the 3-cm band (ν_{micr} = 9290 MHz) at a temperature T = 20°K.

To describe the experimental results we used the following expression for the ENDOR frequencies [5]:

$$h\nu = h\nu_L \pm \frac{1}{2}[a + b(3\cos^2\alpha - 1)], \qquad (1)$$

where ν_L is the nuclear Larmor frequency, a and b are the constants of the isotropic and anisotropic interaction, respectively, α is the angle between the constant magnetic field H_0 and the direction of the defect-nucleus, and the sign ± corresponds to the value of the electron spin projection on the quantization axis (sum and difference frequencies).

The sample was rotated in the (001) plane. The angle Φ between the crystallographic axis [100] and the magnetic field H_0 was varied in the range 0 - 45°.

We observed in the experiment ENDOR near the Larmor frequency of the K^{39} nuclei (ν_L = 0.661 MHz). The symmetrical arrangement of the lines relative to this frequency has made it possible to determine the sum and difference frequencies. The angular dependence of the lines, both sum and difference, could be traced clearly in the entire range of angles, and corresponded to the spheres whose nuclei lie on the crystallograhic axes. The width of the observed lines was approximately the same and equalled 0.002 MHz. The line was not deformed and its width did not change when the angle was varied. Assuming that the fall-off of the hyperfine interaction when the distance from the vacancy is increased by one lattice constant is stronger than the possible increase due to the oscillation of the wave function, we ascribed the observed lines, in accordance with the values of the constants, to the spheres XXV and XLIX.

We must point out the difficulties and possible ambiguities in the identification of lines of remote spheres, even if their angular dependence is known. Thus, for spheres having C_s symmetry, the tensor of the anisotropic hyperfine interaction is in general not axially symmetrical, and its principal axis τ_3 does not coincide with the direction of the defect-nucleus. In this case the formulas given in [5] are valid; these, unlike (1), contain two additional experimentally determined parameters, the constant b_2 of the anisotropic hyperfine interaction, which characterizes the deviation from axial symmetry, and the angle φ between τ_3 and the nearest crystallographic axis. If b_2 and φ are made to approach zero in the formula, then the angular dependence of the ENDOR lines for such spheres will degenerate into the angular dependence of spheres of nuclei lying on the crystallographic axes. Under the condition

$$b_2 = 0, \quad \varphi = 0, \tag{2}$$

these angular dependences are identical.

If we denote by φ_{nuc} the angle between the direction of the defect-nucleus and the nearest crystallographic axis, then the deviation of τ_3 from the direction of the defect-nucleus can be characterized by comparing the values of φ_{nuc} and φ (say, by their difference). For spheres close to a vacancy and having a symmetry C_s, the experimentally determined φ [3,5] do not differ significantly from φ_{nuc}. With increasing distance from the defect, the interaction between the nucleus and the F-center electron can be regarded, with ever increasing accuracy, as an interaction between two pointlike magnetic dipoles. Then we can apparently assume with sufficient degree of accuracy, for remote spheres, that $b_2 = 0$ and $\varphi = \varphi_{nuc}$, i.e., assume that axial symmetry takes place and τ_3 coincides with the direction of the defect-nucleus.

Taking the foregoing into account, we used formula (1) to plot, on the basis of the measured constants, the possible line spectrum at certain angles Φ for spheres with small φ_{nucl}, and compared them with the experimentally observed ones. It turned out that no spheres other than XXV and XLIX could be used to explain the experimentally observed picture of the ENDOR lines. However, one cannot exclude the possibility that one of the investigated spheres may be a closer sphere with small φ_{nuc}, if the deviation of τ_3 from the direction of the

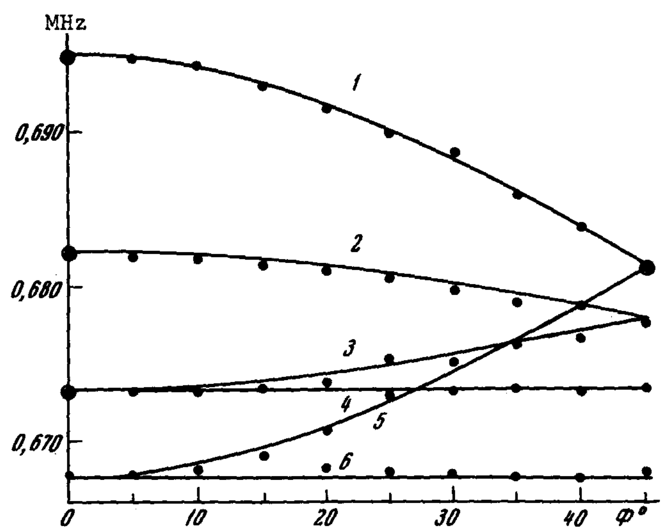

Fig. 1. Angular dependence of the summary ENDOR frequencies of K^{39} nuclei of spheres XXV and XLIX. The solid lines show the theoretical curves, and the points the experimental data. Lines 1,5,6 - sphere XXV, lines 2,3,4 - sphere XLIX. The circled points are those from which the constants were determined.

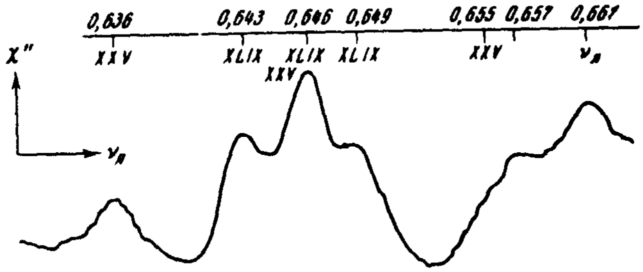

Fig. 2. Spectrum of ENDOR difference lines of K^{39} nuclei of spheres XXV and XLIX, $\Phi = 35°$, χ - imaginary part of the paramagnetic susceptibility, ν_{nuc} - frequency of radiofrequency incident radiation. The number of the sphere to which the line belongs is indicated under the frequency markers.

Hyperfine interaction constant of F center in KCl with nuclei of spheres XXV and XLIX

Sphere	Constant	Value of constant, MHz
XXV	a	0.030
	b	0.018
XLIX	a	0.029
	b	0.006

defect-nucleus is sufficiently large for this sphere.

The fact that we were unable to observe lines from spheres located closer to a vacancy, but whose nuclei were located far enough from the crystallographic axes, is apparently due to the strong localization of the wave function along a direction such as [100].

Near the line marked 2 in Fig. 1 we observed at $\Phi = 0°$ still another ENDOR line. This line, as well as a few poorly resolved lines near the nuclear Larmor frequency of K^{39}, could not be identified as yet.

Figure 2 shows the spectrum of the ENDOR lines of the K^{39} nuclei of spheres XXV and XLIX at $\Phi = 35°$.

The measured constants are listed in the table.

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* Problems involved in the identification of the spheres are discussed at the end of this communication.