ELECTRON NUCLEAR DOUBLE RESONANCE OF F CENTERS IN KCl

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Hyperfine and quadrupole interactions between KCl F centers and crystal lattice nuclei are studied by the electron nuclear double resonance (ENDOR) technique. The angular dependences of the ENDOR frequencies at liquid nitrogen temperature are investigated in detail for ions of the III–VI, VIII, IXa and XIII shells surrounding the vacancies. Quadrupole splitting in the III shells is detected and measured. A general form of the spin Hamiltonian, in which deviation from axial symmetry is taken into account, is employed to describe the experimental results. All parameters of the spin Hamiltonian are determined.

1. INTRODUCTION

A STUDY of the hyperfine interaction of an impurity center in a crystal by the EPR and ENDOR methods permits an estimate of the distribution of the wave function of a localized electron. In many cases EPR is sufficient for this purpose (at least when it comes to the first two coordination spheres surrounding the defect). For remote coordination spheres, and also in the case of crystals where EPR does not give resolution of the hyperfine structure, the ENDOR is the only method with which to study the hyperfine interaction. Among the latter crystals is KCl, which is the object of our investigation.

It should be noted that KCl is a difficult substance for ENDOR measurements. Compared with other alkali-halide crystals, the KCl lattice ion nuclei have small magnetic moments, causing a weak intensity and a strong overlap of the spectral lines. It is obvious that this explains why the hyperfine interaction of F centers in KCl with the nuclei of the remote coordination spheres was not investigated before, although KCl was investigated in some ENDOR studies.[1-4]

In EPR experiments on F centers in KCl, an inhomogeneously broadened single line is observed, whose shape is governed by the hyperfine interaction of the localized electron with the surrounding nuclei of the lattice ions. Apparently the main contribution to the line shape is made by the interaction with the nuclei of coordination spheres I and II.

The present paper reports the most complete investigation of the hyperfine interaction of F centers in KCl. We studied in detail the angular dependences of the ENDOR frequencies for the nuclei of the coordination spheres[1)] III–VI, VIII, IXa, and XIII. The high resolution and precision of the measurements have made it possible to observe quadrupole splitting even for the coordination sphere III at different crystal orientations relative to the external static magnetic field, something hitherto impossible for any of the investigated alkali-halide crystals.

In comparing theory with experiment, we used the general form of the hyperfine-interaction spin Hamiltonian. The simplification of the latter and the number of independent parameters were dictated by the symmetry of the spin Hamiltonian for nuclei of one coordination sphere or another. We note that a simplified spin Hamiltonian with axial symmetry was used in [4,6] for the data reduction. Our results show that a correct comparison of theory with experiment is possible only when a general spin Hamiltonian, reflecting the concrete form of the problem, is used. The experimental results are tabulated in Sec. 4.

2. EXPERIMENTAL PROCEDURE AND TECHNIQUE

We used for the measurements KCl single crystals with F-center concentration 10^{17} cm^{-3} (by optical measurement). The F centers were obtained by additive coloring. The investigations were made with a superheterodyne ENDOR spectrometer operating in the 3 cm band (ν_{SHF} = 9260 MHz)[5] at 77° K. The sample was rotated in the (001) plane.

[1)]The results of measurements for the nuclei of coordination spheres I and II were reported in an earlier paper [5]. Sphere IXa (in Doyle's definition [6]) is the sphere [300], as distinguished from the sphere IXb–the sphere [221].

A cryostat that permitted operation without cooling the resonator was used for the low-temperature measurements. The sample was in vacuum and secured to a rod soldered to the internal vessel with the cooling liquid. A quartz stub, inside which the investigated crystal was placed, was joined to the body of the cryostat and ensured that the sample was in vacuum. The internal vessel was communicated with the main body through a ground joint that made rotation of the sample possible. The angle of rotation was read against a dial graduated in 1° divisions. The orientation of the crystal in the external static magnetic field was by means of the ENDOR spectra. In view of the low Larmor frequencies of the nuclei K and Cl, more stringent requirements were imposed on the long-term stability of the magnetic field. The magnetic field was monitored continuously during the experiment with an NMR transmitter.

3. THEORY

The spin Hamiltonian of an arbitrary lattice nucleus in an external static magnetic field, with account of the hyperfine interaction with localized electron, is written as follows:

$$\hat{\mathcal{H}} = -\frac{\mu_{nuc}}{I}\mathbf{H}\hat{\mathbf{I}} + a\hat{\mathbf{I}}\hat{\mathbf{S}} + \sum_{pq} D_{pq}\hat{I}_p\hat{S}_q, \qquad (1)$$

where the constant a of the isotropic hyperfine interaction is equal to

$$a = \frac{8\pi}{3}\frac{\mu\mu_{nuc}}{SI}|\psi(\rho = 0)|^2 \qquad (2)$$

(ψ is the wave function of the localized electron), and the component of the tensor of the anisotropic hyperfine interaction is

$$D_{pq} = \frac{\mu\mu_{nuc}}{SI}\int |\psi|^2 \frac{3x_p x_q - \delta_{pq}\rho^2}{\rho^5}\,dV. \qquad (3)$$

We use a local system of coordinates with origin at the nucleus; ρ is the radius vector of the electron; S, I, μ, and μ_{nuc} are respectively the spins and magnetic moments of the electron and nucleus; p and q number the Cartesian axes of the coordinate system. The coordinate system in which the symmetrical tensor D_{pq} is diagonal will be called principal, and its axes will be denoted by τ_1, τ_2, and τ_3.

Diagonalizing the spin Hamiltonian, we use the strong field condition

$$g_e\mu H_0 \gg a, b, \qquad (4)$$

which is well satisfied in our case. The corrections of second order in perturbation theory can then be neglected. For the case when the simplifying symmetry group[7] contains an axis of order not lower than threefold, the frequencies of the ENDOR transitions are written in the general form as[2)]

$$h\nu = g_{nuc}\beta_{nuc}H_0 \pm {}^1/_2[a + b(3\cos^2\alpha - 1)], \qquad (5)$$

where $b = D_{33}$, α is the angle between the τ_3 axis and the external static magnetic field $\mathbf{H}_0$ and β_{nuc} is the nuclear magneton.

The plus and minus signs correspond to the value of the electron spin projection on the quantization axis (sum and difference frequencies). In this case the τ_3 axis is directed along the symmetry axis, which coincides with the defect–nucleus direction, and the choice of the two other axes in the plane perpendicular to τ_3 is arbitrary. The corrections pointed out by Zevin[7] (and which play an important role when $a \approx b$) are negligibly small in our case.

Formula (5) was used to describe the angular dependences of the ENDOR frequencies of the coordination spheres I, III, IV, and IXa. Allowance for the quadrupole interaction leads to an additional term in formula (5)[1]

$$\Delta = Q(3\cos^2\alpha - 1)(m_I - {}^1/_2), \qquad (6)$$

where Q is the quadrupole interaction constant and m_I is the eigenvalue of the nuclear spin operator projection. In (6) it is necessary to substitute the larger of the two values corresponding to the transition with $\Delta m_I = \pm 1$.

If a symmetry axis lower than threefold or a symmetry plane exists, the ENDOR transition frequencies are written in the form

$$h\nu = g_{nuc}\beta_{nuc}H_0 \pm {}^1/_2[a + b_1(3\cos^2\alpha - 1) + b_2(3\cos^2\beta - 1)],$$

$$b_1 = -{}^1/_3(D_{11} + 2D_{22}), \qquad b_2 = {}^1/_3(D_{11} - D_{22}), \qquad (7)$$

where β is the angle between $\mathbf{H}_0$ and the τ_1 axis.

If the simplifying symmetry group is C_{2v}, the τ_3 axis is directed along the symmetry axis and τ_1 and τ_2 lie in the v-planes (the coordination spheres II and VIII).

For group C_3, the τ_2 axis is directed perpendicular to the plane, and τ_1 and τ_3 lie in the symmetry plane. The spatial position of τ_3 is determined by the angle φ between the nearest crystallographic axis and τ_3 (see Fig. 1). The expressions for the frequencies are in this case rather simple. However, the deviation from axial symmetry is characterized more illustratively by the angle θ, which is connected with φ by

[2)] This notation corresponds to the case of remote spheres, when $g_{nuc}\beta_{nuc}H_0 > a, b$.

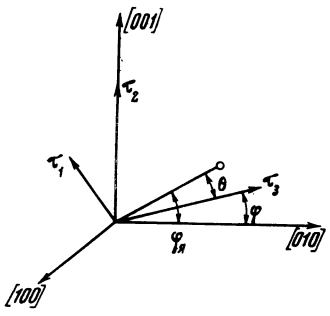

FIG. 1. Spatial orientation of the principal axis of the hyperfine interaction tensor for the symmetry group C_s. O–the lattice nucleus under consideration.

$$\theta = \varphi_{nuc} - \varphi, \tag{8}$$

where φ_{nuc} is the angle between the direction to the nucleus and the nearest crystallographic axis. In the case of axial symmetry $\theta = 0$.

In Table I are listed the formulas for the ENDOR sum frequencies for spheres III, V, and VI. Here $C = g_{nuc}\beta_{nuc}H_0 + \frac{1}{2}(a - b_1 - b_2)$; Φ is the angle between $\mathbf{H}_0$ and the [100] axis. The expressions for the frequencies of the coordination spheres I and II were given in [5]. The formulas for spheres IV and IXa are similar to the formulas for sphere I, the formulas for sphere VIII are similar to the formulas for sphere II, and those for sphere XIII are similar to formulas for sphere V.

4. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Sphere III. Figure 2 shows the angular dependence of the ENDOR frequencies for K^{39} nuclei of coordination sphere III. In this and following figures, the solid lines are the theoretical curves, and the points represent the experimental data.

The theory contains three parameters: a, b, and Q. They were determined point by point for $\Phi = 45°$ (the points from which the constants were determined are marked by circles on this and on the other figures). The quadrupole splitting becomes noticeable at $\Phi = 15°$ and increases with increasing angle.

Figure 3 shows the ENDOR spectrum of coordination sphere III (sum frequencies). Difference frequencies were also observed. The intensity of the different-frequency spectrum was somewhat lower. The spectra of the sum and difference frequencies are symmetrically disposed relative to the Larmor frequency of the K^{39} nuclei (ν_L = 0.66 MHz). Such a symmetrical arrangement is characteristic of all of the coordination spheres of the F center in KCl above sphere II. Allowance for this property helps interpret the complex spectra of the remote coordination spheres.

Table I. Angular dependences of ENDOR frequencies.

Formulas	Direction to nucleus
Coordination sphere III	
$h\nu_{1,2} = g_{nuc}\beta_{nuc}H_0 + a/2 + \frac{1}{2}b\sin 2\Phi \pm Q\sin 2\Phi$ $h\nu_3 = g_{nuc}\beta_{nuc}H_0 + a/2 + \frac{1}{2}b\sin 2\Phi$	[111], [11$\bar{1}$]
$h\nu_{4,5} = g_{nuc}\beta_{nuc}H_0 + a/2 - \frac{1}{2}b\sin 2\Phi \pm Q\sin 2\Phi$ $h\nu_6 = g_{nuc}\beta_{nuc}H_0 + a/2 - \frac{1}{2}b\sin 2\Phi$	[1$\bar{1}$1], [1$\bar{1}\bar{1}$]
Coordination sphere V	
$h\nu_1 = C + \frac{3}{2}[b_1\sin^2(\varphi+\Phi) + b_2\cos^2(\varphi+\Phi)]$	[120]
$h\nu_2 = C + \frac{3}{2}[b_1\cos^2(\varphi-\Phi) + b_2\sin^2(\varphi-\Phi)]$	[210]
$h\nu_3 = C + \frac{3}{2}[b_1\cos^2(\varphi+\Phi) + b_2\sin^2(\varphi+\Phi)]$	[$\bar{2}$10]
$h\nu_4 = C + \frac{3}{2}[b_1\sin^2(\varphi-\Phi) + b_2\cos^2(\varphi-\Phi)]$	[$\bar{1}$20]
$h\nu_5 = C + \frac{3}{2}[b_1\cos^2\varphi + b_2\sin^2\varphi]\sin^2\Phi$	[021], [02$\bar{1}$]
$h\nu_6 = C + \frac{3}{2}[b_1\sin^2\varphi + b_2\cos^2\varphi]\sin^2\Phi$	[012], [01$\bar{2}$]
$h\nu_7 = C + \frac{3}{2}[b_1\sin^2\varphi + b_2\cos^2\varphi]\cos^2\Phi$	[102], [10$\bar{2}$]
$h\nu_8 = C + \frac{3}{2}[b_1\cos^2\varphi + b_2\sin^2\varphi]\cos^2\Phi$	[201], [20$\bar{1}$[
Coordination sphere VI	
$h\nu_1 = C + \frac{3}{4}(b_1\sin^2\varphi + b_2\cos^2\varphi)(\cos\Phi + \sin\Phi)^2$	[112], [11$\bar{2}$[
$h\nu_2 = C + \frac{3}{4}(b_1\sin^2\varphi + b_2\cos^2\varphi)(\cos\Phi - \sin\Phi)^2$	[1$\bar{1}$2], [1$\bar{1}$2]
$h\nu_3 = C + \frac{3}{4}[b_1(\sin\varphi\cos\Phi - \sqrt{2}\cos\varphi\sin\Phi)^2 + b_2(\cos\varphi\cos\Phi + \sqrt{2}\sin\varphi\sin\Phi)^2]$	[1$\bar{2}$1], [1$\bar{2}\bar{1}$]
$h\nu_4 = C + \frac{3}{4}[b_1(\sin\varphi\cos\Phi + \sqrt{2}\cos\varphi\sin\Phi)^2 + b_2(\cos\varphi\cos\Phi - \sqrt{2}\sin\varphi\sin\Phi)^2]$	[121], [12$\bar{1}$]
$h\nu_5 = C + \frac{3}{4}[b_1(\sin\varphi\sin\Phi + \sqrt{2}\cos\varphi\cos\Phi)^2 + b_2(\cos\varphi\sin\Phi - \sqrt{2}\sin\varphi\cos\Phi)^2]$	[21$\bar{1}$], [211]
$h\nu_6 = C + \frac{3}{4}[b_1(\sin\varphi\sin\Phi - \sqrt{2}\cos\varphi\cos\Phi)^2 + b_2(\cos\varphi\sin\Phi + \sqrt{2}\sin\varphi\cos\Phi)^2]$	[2$\bar{1}$1], [2$\bar{1}\bar{1}$]

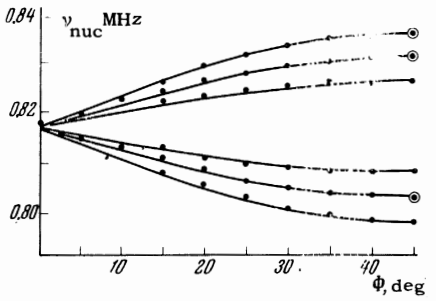

FIG. 2. Angular dependence of the ENDOR frequencies for the K^{39} nuclei of coordination sphere III as the sample is rotated in the (001) plane.

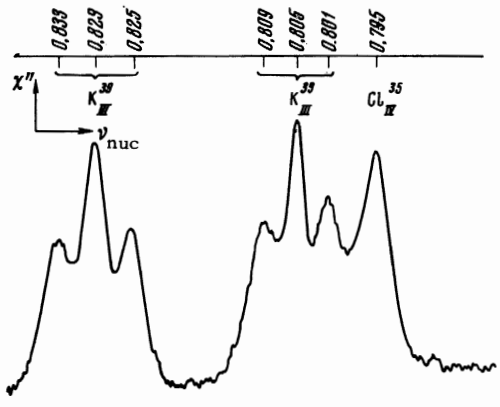

FIG. 3. ENDOR spectra of the coordination sphere III, $\Phi = 30°$; χ''–imaginary part of the considered susceptibility, ν_{nuc}–frequency of superimposed rf illumination.

Spheres IV, VI, VIII. Figure 4 shows the angular dependence of the ENDOR frequencies for the Cl^{37} nuclei of coordination sphere IV. The inversion of the sum and difference frequencies is clearly seen. The lines of sphere IV are quite intense and are observed even at room temperature.

The sum frequencies of the isotope Cl^{35} are strongly overlapped by the difference frequencies

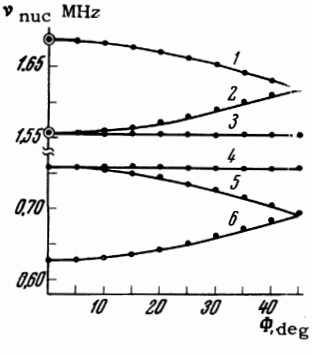

FIG. 4. Angular dependence of the summary and difference frequencies of ENDOR for the nuclei Cl^{37} of the coordination sphere IV; curves 1–3) sum frequencies, 4–6) difference frequencies

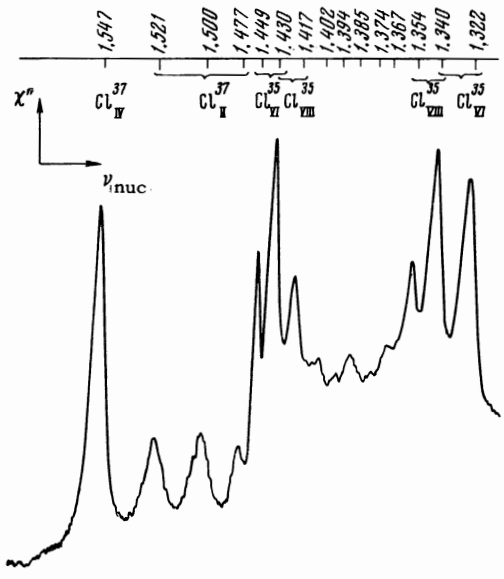

FIG. 5. ENDOR spectrum of coordination spheres IV, VI, and VIII; $\Phi = 0°$.

of sphere II. The difference frequencies of Cl^{35} at certain angles overlap the spectra of spheres III, V, IXa, and XIII, but they can be traced relatively easily because of the strong angular dependence. Figure 5 shows the ENDOR spectrum of the coordination spheres IV, VI, and VIII. It is interesting to note that at 1.385 MHz (region of Larmor frequency for the Cl^{35} nuclei), a characteristic absorption burst is observed, due apparently to the remote spheres. Several other lines, whose angular dependence can barely be traced, can be seen symmetrically on both sides of the Larmor frequency. These are most probably connected with spheres X or XVI. In Table II the constants for these lines are conditionally listed under sphere X.

The angular dependence of the coordination sphere VI is best traced by means of the difference frequencies. Figure 6 shows the angular dependence of the difference frequencies of ENDOR

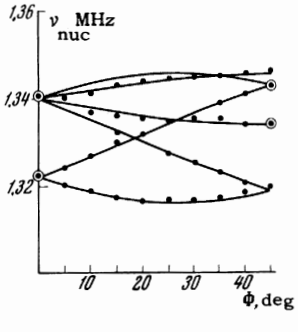

FIG. 6. Angular dependence the ENDOR difference frequenci of coordination sphere VI.

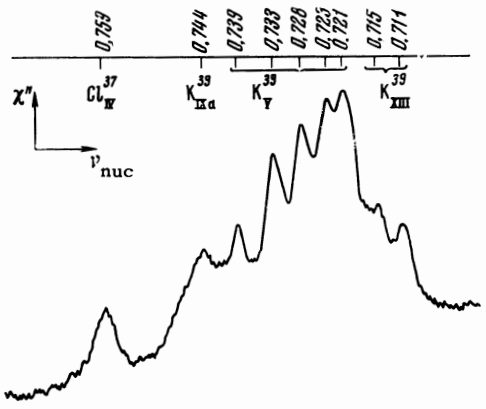

FIG. 7. ENDOR spectrum of coordination spheres V, IXa, and XIII, $\Phi = 30°$.

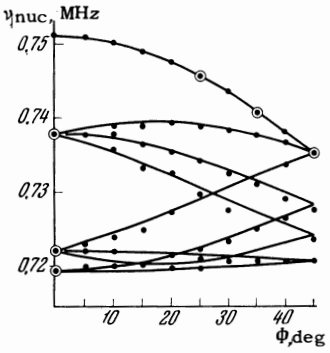

FIG. 8. Angular dependence of the ENDOR frequencies for the K^{39} nuclei of coordination spheres V, and IXa (upper line).

for coordination sphere VI. From a comparison of dependence of the observed lines has made it possible to identify the spheres IXa and XIII.

The lines of coordination spheres IXb and XI were not observed. They are either completely overlapped by the lines of the coordination spheres theory with experiment we were able to determine for it a small deviation from axial symmetry ($\theta = 1°$).

The angular dependence of sphere VIII is similar to the angular dependence of sphere II. One observes well in the experiment only two lines of sphere VIII, at certain angles. Nonetheless, it turns out to be possible to determine the constants a and b. We note that the scatter in the values of a as determined from different points is insignificant, whereas for b it is large.

Spheres V, IXa, XIII. Figure 7 shows one of the typical ENDOR spectra characteristic of coordination spheres V, IXa, and XIII. Figure 8 illustrates the angular dependence of the ENDOR lines of sphere V and one of the lines of sphere IXa. All other lines of sphere IXa are inside the group of lines of sphere V, increasing their intensity; they are not resolved.

The ENDOR lines of sphere V strongly overlap both each other and lines of other spheres. The small value of the constants b_1 and b_2 (weak contribution of the anisotropic interaction) makes it impossible to trace some of the lines in the entire range of angles from 0 to 45°. The description of the experimental angular relations is possible only when account is taken of the deviation from axial symmetry (the theory contains four parameters a, b_1, b_2, θ). In this case $\theta = 90°$ and the deviation from axial symmetry is appreciable.

Above and below the lines of sphere V one observes lines of spheres IXa and XIII. The angular V, IXa, XIII and do not appear for any of the crystal orientations (this is possible if they are sufficiently weak in intensity compared with the lines of the indicated spheres), or else are characterized by small values of a and b and are located in the region of the Larmor frequency of the K^{39} nuclei; we were unable to observe them in a thorough investigation of this region.

We can state that for like ions the constant a and consequently also $|\psi|^2$, has a nonmonotonic dependence on the number of the sphere. Thus, the constant of sphere IXa is larger than that of sphere V. The explanation for this must apparently be sought either in the complex structure of the conduction band,[8,9] or in the presence of a "cubic" component of the wave function of F-center electron. Table II lists, besides the results of our measurements, also results by others and the values of $|\psi|^2$ at the lattice site, as calculated from our data.

In conclusion we note that our data on the ENDOR of F centers in KCl correlate with the results of Seidel for NaCl[3] and of Doyle for NaF.[6] The deviation from axial symmetry in NaCl is identical with that obtained by us in KCl. The peak of the constant a, observed by Doyle for sphere IXa, is likewise characteristic. The angular dependences given in [6] likewise reveal deviation from axial symmetry. The foregoing estimates show that it is of the order of 9° for the sphere V.

Kubler and Fraiauf[10] used the method of Gourary and Adrian[11] to calculate the wave functions of the remote coordination spheres in KCl and NaF crystals. The appreciable disparity between our results and the results of [10] points to the need for refining the theory so as to obtain more accurate wave functions for the remote coordination spheres.

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Table II. Constants of F-center hyperfine structure in KCl.

Sphere	Type of nucleus	Constant*	Literature data $T = 1,2°$ K		Our measurements		
			Value of constant	Reference	Value of constant	$\|\psi\|^2$, at. un.	T, °K
I	K^{39}	a	21,6	[1]	21,28	0.102074	300
		b	0.95		1,08		
		Q	0,20		0.20		
II	Cl^{35}	a	7.0	[1]	7.08	0.016180	300
		b_1	0,50		0,510		
		b_2	—		0,010		
		Q_{11}	0,064		0,055		
		Q_{22}	0,090		0,087		
III	K^{39}	a	0,31	[4]	0.3140	0.001506	77
		b	0.032		0,0280		
		Q	—		0,0050		
IV	Cl^{35}	a	1.06	[4]	1,0510	0.002401	77
		b	0.11		0,1060		
IV	Cl^{37}	a	—		0,8760		77
		b	—		0,0880		
V	K^{39}	a	—		0,1332	0,000639	77
		b_1	—		0,0135		
		b_2	—		0,0007		
		θ	—		9		
VI	Cl^{35}	a	0,10	[4]	0.1020	0.000233	77
		b_1	0,03		0,0240		
		b_2	—		0.0004		
		θ	—		1		
VIII	Cl^{35}	a	—		0.0810	0.000185	77
		b	—		0.0180		
IXa	K^{39}	a	—		0.1430	0.000686	77
		b	—		0,0200		
X	Cl^{35}	a	—		0,0220	0,000050	77
		b	—		0,0076		
XIII	K^{39}	a	—		0.1240	0,000595	77
		b_1	—		0,0274		
		b_2	—		0.0006		
		θ	—		5		

*Constants a, b, and Q given in MHz, θ in degrees.

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120