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# Phase Transitions in $\text{KJO}_3$ Detected by NQR

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## *Résumé.*

Les raies de résonance quadripolaire des transitions  $\pm 3/2 \leftrightarrow \pm 1/2$  de  $\text{J}^{127}$  en  $\text{KIO}_3$  ont été mesurées en fonction de la température entre  $20^\circ$  et  $280^\circ$  C. La structure cristalline a été étudiée par la méthode de Debye-Scherrer entre  $20^\circ$  et  $400^\circ$  C. En résonance quadripolaire on observe nettement deux transitions de phase à  $75^\circ$  et  $220^\circ$  C, qui ne se manifestent que faiblement aux rayons X. La symétrie du cristal augmente à température croissante, le cristal étant trigonal au-dessus de  $220^\circ$  C. Toutes les phases sont piézoélectriques.

Giebe-Scheibe measurements by Hettich [1] indicated a phase transition in  $\text{KJO}_3$  at  $+150^\circ$  C. Ludwig [2] observed 3 closely spaced quadrupole resonance frequencies at room temperature in this substance.

We have measured the NQR-frequencies of the  $\pm 1/2 \leftrightarrow \pm 3/2$  transitions of  $\text{J}^{127}$  in  $\text{KJO}_3$  from room temperature up to  $285^\circ$  C at intervals of about  $10^\circ$  C. The apparatus consisted of a simple self-quenched super-regenerative LC-oscillator with a one half turn coil. Zeeman modulation and lock-in detection provided a good sensitivity. The construction of the thermostat offered some difficulties, since a temperature inhomogeneity of  $3^\circ$  C over the sample (1" in diameter) extinguished the quadrupole resonances by broadening. A flowing-gas system proved to be completely insufficient. Good results were obtained by immersing the sample together with the coil in a heated and well stirred paraffine oil bath, but the paraffine vapours were somewhat inconvenient at higher temperatures. An unexpected but very good success was finally obtained with a carefully designed cylindrical furnace (1,5" diameter, 1,5" long). The two closely fitting brass shells were completely covered by the heating coils on the outside. The connections between the rf-coil inside the furnace and the oscillator were teflon insulated and made of very thin copper foil to minimize inhomogeneity-causing thermal leaks.

At  $20^\circ\text{C}$  we observed the 3 lines reported by Ludwig at (a) 145,7, (b) 145,2 and (c) 144,7 MHz with signal-to-noise ratios of (a) 60, (b) 90, (c) 35 and a fourth additional line at (d) 144,2 MHz with  $\text{S}/\text{N} \sim 10$ . With increasing temperature, all these frequencies decrease linearly with the same temperature coefficient  $d\nu/dT = -27 \text{ kHz/grad}$ . The intensity of the lines (a), (b), (c) decreases rapidly until they disappear at  $\sim 75^\circ\text{C}$  whereas (d) increases at this temperature to a  $\text{S}/\text{N} \sim 200$ , then falling slowly again. Above  $170^\circ\text{C}$  the frequency variation deviates from linearity, bending to lower frequencies. At  $220^\circ\text{C}$  the line disappears, but above this temperature it grows rapidly to a  $\text{S}/\text{N} \sim 100$ . It shows then a nearly constant intensity and a temperature coefficient  $d\nu/dT = -13,5 \text{ kHz/grad}$  up to  $285^\circ\text{C}$ . At this temperature the resonance frequency is 136,7 MHz. There was also an annealing effect observed since the  $\text{S}/\text{N}$  at room temperature were (a) 70, (b) 90, (c) 8 and (d) 7 after heating to this temperature. The line width of all the lines is  $\sim 100 \text{ kHz}$ . The possible error of frequency is  $\pm 0,1 \text{ MHz}$ , that of temperature  $\pm 2^\circ\text{C}$ .

In order to check Hettich's observations, we have also reexamined the ultrasonic (mechanical) resonances of microcrystalline  $\text{KJO}_3$  powder. This can be done simply by placing a few grains of the powder in a small condenser ( $\sim 1 \text{ pF}$ ) which is connected in parallel to the tuning capacitor of a frequency-modulated nuclear resonance apparatus [3]. In the region of 10 MHz, a great number of lines were recorded at room temperature with a temperature coefficient  $d\nu/dT = -4 \cdot 10^{-4}/\text{grad}$ . This coefficient changes to  $-1,6 \cdot 10^{-3}/\text{grad}$  at  $75^\circ\text{C}$  and then reverses its sign, the intensity of the lines decreasing until they disappear at  $85^\circ\text{C}$ . Between  $80^\circ\text{C}$  and  $220^\circ\text{C}$  there are only few lines with a temperature coefficient of  $+5 \cdot 10^{-4}/\text{grad}$ . At  $+150^\circ\text{C}$  some of the lines will disappear and others appear, but this seems not to be a significant effect. Above  $220^\circ\text{C}$  a very great number of lines appears. This may be partly due to a fracturing of the crystals since after heating to this temperature the room temperature spectrum could no longer be reproduced.

$\text{KJO}_3$  has a pseudocubic perovskite-like structure. Indexing a powder-diagram Naray-Szabo [4] assigned to it a large monoclinic elementary cell with  $a = 8,92 \text{ \AA}$  and  $Z = 8$  (room temperature). It has not yet been possible to grow sufficiently large single crystals. Therefore powder diagrams have been taken from room temperature up to  $400^\circ\text{C}$ , where the specimen decomposed. Above  $220^\circ\text{C}$  the splitting of the powder lines could be analyzed and leads to a trigonal pseudocubic structure

with the following values of the lattice constant and the rhombohedral angle:

Temp. ° C.	$a$ Å	$\alpha$
220	9,012	89° 14,6'
295	9,046	89° 9,0'
350	9,068	89° 4,3'

The large cell ( $Z = 8$ ) follows from the observed superstructure lines.

At temperatures below 220° C the line splitting is but slightly changed, since only some of the trigonal lines show an additional splitting. This can be understood as a lowering of the symmetry with minute deviations from the trigonal high-temperature phase.

#### CONCLUSIONS.

- 1)  $\text{KJO}_3$  exists in three different phases between room temperature and 250° C which show slight differences in X-ray powder diagrams, but which are easily identified by NQR.
- 2) The transition temperatures are 75° C and 220° C. The lower transition is very probably of first order, the upper one of higher order.
- 3) The  $\text{KJO}_3$  crystals are piezoelectric in all three phases, hence the structure cannot have a center of symmetry. There are 3 chemically inequivalent J lattice sites in the room temperature phase, but only one in the high-temperature phases, as follows from the number of NQR lines.
- 4) To obtain further and better information about these phase transitions, single crystal studies of the NQR Zeeman splitting, the dielectric constant and the structure by X-ray diffraction are necessary. Therefore we are trying to grow single crystals of  $\text{KJO}_3$ , which has proved to be very difficult till now.

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