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Phase Transitions in 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 I^{127} en KIO_3 ont été mesurées en fonction de la température entre 20° et 280° C. La structure cristalline a été étudiée par la méthode de Debye-Scherrer entre 20° et 400° C. En résonance quadripolaire on observe nettement deux transitions de phase à 75° et 220° 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° C. Toutes les phases sont piézoélectriques.

Giebe-Scheibe measurements by Hettich [1] indicated a phase transition in KJO_3 at + 150° 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 J^{127} in KJO_3 from room temperature up to 285° C at intervals of about 10° C. The apparatus consisted of a simple self-quenched superregenerative 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° 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° 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 S/N $\sim$ 10. With increasing temperature, all these frequencies decrease linearly with the same temperature coefficient $d\nu/dT = -27$ kHz/grad. The intensity of the lines *(a)*, *(b)*, *(c)* decreases rapidly until they disappear at $\sim$ 75° C whereas *(d)* increases at this temperature to a S/N $\sim$ 200, then falling slowly again. Above 170° C the frequency variation deviates from linearity, bending to lower frequencies. At 220° C the line disappears, but above this temperature it grows rapidly to a S/N $\sim$ 100. It shows then a nearly constant intensity and a temperature coefficient $d\nu/dT = -13{,}5$ kHz/grad up to 285° C. At this temperature the resonance frequency is 136,7 MHz. There was also an annealing effect observed since the S/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 kHz. The possible error of frequency is $\pm$ 0,1 MHz, that of temperature $\pm$ 2° C.

In order to check Hettich's observations, we have also reexamined the ultrasonic (mechanical) resonances of microcrystalline KJO_3 powder. This can be done simply by placing a few grains of the powder in a small condenser ($\sim$ 1 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 $d\nu/\nu dT = -4 \cdot 10^{-4}$/grad. This coefficient changes to $-1{,}6 \cdot 10^{-3}$/grad at 75° C and then reverses its sign, the intensity of the lines decreasing until they disappear at 85° C. Between 80° C and 220° C there are only few lines with a temperature coefficient of $+5 \cdot 10^{-4}$/grad. At + 150° C some of the lines will disappear and others appear, but this seems not to be a significant effect. Above 220° 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.

KJO_3 has a pseudocubic perovskite-like structure. Indexing a powder-diagram Naray-Szabo [4] assigned to it a large monoclinic elementary cell with $a = 8{,}92$ Å 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° C, where the specimen decomposed. Above 220° 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	α
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) 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 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 KJO_3, which has proved to be very difficult till now.

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