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The Chlorine Nuclear Quadrupole Resonance of *o*-, *m*-, and *p*-Chlorobenzamide

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The nuclear quadrupole resonance of *o*-, *m*-, and *p*-chlorobenzamide has been studied in this laboratory; the results and their relation to the crystal structures of these materials, the various polymorphic modifications of which have been extensively studied by Sakurai, Takaki, and others,[1] will be reported in this paper.

The materials were synthesized by the reaction of monochlorobenzoic acid with thionyl chloride and then with ammonia. No impurity was seen in the X-ray powder diffraction patterns or in the infrared spectra of the materials purified by repeated recrystallization from the various solvents mentioned below. The melting points of the final samples are shown in Table 1. These samples were sealed *in vacuo* in glass ampules for the NQR measurement. We were not successful in growing a single crystal for the Zeeman measurement.

The NQR signal was searched for in the range from 28 to 40 MHz using a super-regenerative oscillator-detector of the Dean type with a frequency-modulation and phase-sensitive detection system. The S/N ratio of the signal of *p*-dichlorobenzene was better than 200 with this system. The frequency was determined with an eight-figure digital counter. For the visual detection, a Braun tube with a long decay time was employed, and the random noise was fairly well smoothed out with the S/N ratio—about five times better than that of an ordinary tube. The resonance frequencies observed are shown in Table 1 and Fig. 1.

Table 1.

	Mp, °C	Space group	NQR frequency at 77K, MHz	S/N
o-chlorobenzamide	142.3	$P2_1/a$	35.593	3
m-chlorobenzamide	132.0	$P2_1/a$	34.876	3
p-chlorobenzamide	177.6	$P\bar{1}$	35.130	3
			34.944	2.5
			34.731	2.5

The thermal behavior of these materials between −100°C and their melting points was studied by means of a differential scanning calorimeter of the Rigakudenki Co., 8001 SC, with a heating and cooling rate of 10°C/min and with a sensitivity of 0.5 mcal/sec in full scale. About 10 mg of each sample was placed in a shallow aluminum dish, covered with an aluminum plate or packed with pressure, and then used for the DSC measurement.

1) o-*Chlorobenzamide.* One NQR signal was observed with the crystal grown from the melt, but no signal was detected with the crystals grown from water, ethanol, or acetone. The X-ray study[1] showed that the former crystal belonged to the space group $P2_1/a$ with $Z=4$ and had an ordered structure, while the latter ones seemed to be mixtures of three modifications, one with the space group $P2_12_12_1$ and two with some disordered structures. The crystallographically-equivalent chlorine atom in the unit cell is expected to be one in the former case; this agrees with our findings. The reason for the absence of the NQR signal in the latter case may be that the sample was a mixture of different crystal modifications, two of which have disordered structures. No thermal anomaly was detected with any of these crystals.

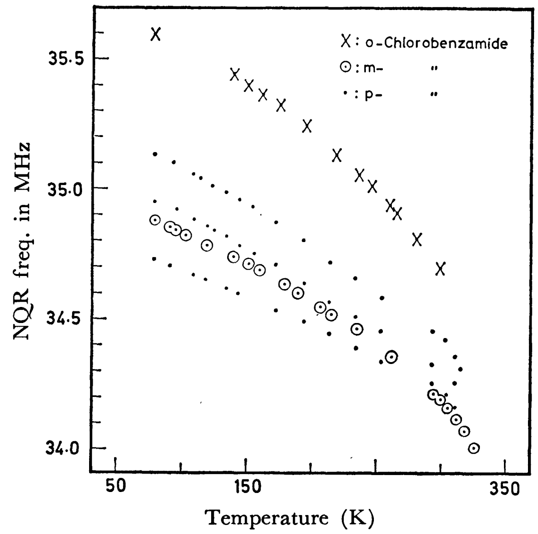

Fig. 1. Frequency *versus* temperature curves of the NQR frequencies of *o*-, *m*-, and *p*-chlorobenzamide.

2) m-*Chlorobenzamide.* The crystals grown from the melt and from water or ethanol possess the same space group, $P2_1/a$, with $Z=4$ according to the X-ray study.[1] These crystals showed only one signal each, all of the same frequency. The crystallographic consideration of this structure described in section 1 agrees with those NQR results. No anomalous thermal behavior was observed in this study with these crystals.

3) p-*Chlorobenzamide.* Three signals were observed with the crystal grown from the melt in the temperature range from 77 K to about 316 K. This finding agrees well with the crystallographic consi-

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[1] Y. Harada, T. Taniguchi, Y. Takaki, and K. Sakurai, *Mem. Osaka Kyoiku University*, **18**, *Ser.* III, 1 (1969); Y. Kato, Y. Takaki, and K. Sakurai, Symposium on the Molecular Structure, Chem. Soc. Japan, 1970.

derations that the crystal at room temperature possesses the space group $P\bar{1}$ with $Z=6$[1] and the three different electric fields are supposed to surround the chlorine atoms in this unit cell. A phase transition from the room-temperature phase to the phase with the same space group and $Z=2$ was found at about 43°C by the X-ray study[1]; this was confirmed by DTA measurements.[2] The six molecules in the unit cell of the low-temperature phase displace a small amount at the phase transition, and the crystal assumes a disordered structure. The periodicity or the length of the *a*-axis of the unit cell of the high-temperature phase decreases to one third of that of the low-temperature phase, while the lengths of the *b*- and *c*-axes are kept the same, with a small entropy of transition (about 0.40 e. u., according to the present DSC measurement). The temperature coefficient of the curves of the NQR frequencies of this material against the temperature in Fig. 1 increases gradually near the transition point; these signals fade out at the transition point, 43°C. This result suggests that the thermal motion of the molecule in the low-temperature phase begins to increase near the transition temperature and that this thermal motion and the disorder of the structure of the upper phase[1] make it impossible to observe the signal above the phase transition. The signal frequencies of these three compounds have values similar to those of other monochlorobenzene derivatives. The frequency of *o*-chlorobenzamide has the highest value and, therefore, the largest covalent character of the C–Cl bond.

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[2] T. Koide, private communication.