INVESTIGATION OF STATISTICALLY DISORDERED SYSTEMS BY THE METHOD OF NUCLEAR QUADRUPOLE RESONANCE

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INVESTIGATION OF STATISTICALLY DISORDERED SYSTEMS BY THE METHOD OF NUCLEAR QUADRUPOLE RESONANCE

GROWTH OF ORDERED CRYSTALS OF *p*-NITROCHLOROBENZENE ON CRYSTALLINE "MATRICES" OF *p*-BROMO- AND *p*-IODONITROBENZENES

(Presented by Academician I. V. Obreimov, November 17, 1965)

In works ([1]–[6]) it was shown that the appearance of statistical disorder in molecular crystals corresponds to a sharp broadening of the lines of nuclear quadrupole resonance (NQR).

The investigation of *p*-nitrochlorobenzene by the NQR method ([2])* with the aid of a pulsed spectrometer made it possible to assert that the orientations of the molecules of this substance in the crystal are statistically disordered. Spectrally this is manifested in the appearance of a broad (~350 kHz) NQR line of Cl^{35} at the frequency 34.88 MHz.

The previously studied ([8]) NQR spectra of Br^{79} and I^{127} of *p*-bromo- and *p*-iodonitrobenzenes contained only narrow lines, which indicated a high degree of ordering of the crystals of these substances. It should be noted: *p*-bromo- and *p*-iodonitrobenzenes, which are isomorphous with one another ([9], [10]), are not isomorphous with *p*-nitrochlorobenzene ([7]), although one of the lattice parameters of all three compounds is close in magnitude.

The closeness of the shapes and sizes of the molecules of this series of halonitrobenzenes and the presence in them of fairly large dipole moments made it possible to hope that, with a suitable choice of conditions, epitaxial growth of ordered crystals of *p*-nitrochlorobenzene would prove possible; i.e., it was expected that on the surface of crystals of *p*-bromo- and *p*-iodonitrobenzenes, as on replicas, crystals of the ordered phase of *p*-nitrochlorobenzene would grow.

An attempt to prepare samples for investigation by deposition from a solution of mixtures of *p*-nitrochlorobenzene with *p*-bromo- or *p*-iodonitrobenzene was unsuccessful—the NQR line still remained broad, i.e., orientation did not occur.

Subsequently, for the preparation of samples, the method of zone melting of the corresponding mixtures was chosen. With the aid of zone melting, an impurity gradient was produced along the samples, which made it possible to examine qualitatively the dependence of the orientation process on the content of impurity crystals.

The samples for investigation were obtained as follows: in glass tubes 10 mm in diameter and about 15–16 cm long, mixtures of 20% p-$BrC_6H_4NO_2$ + 80% p-$ClC_6H_4NO_2$ (I) and 30% p-$JC_6H_4NO_2$ + 70% p-$ClC_6H_4NO_2$ (II) were melted. As a control, a sample of pure p-$ClC_6H_4NO_2$ (III) was taken. The mixtures in the tubes were subjected to zone melting for several days. Before the measurements the tubes were broken into equal parts and numbered in such a way that the greatest impurity content

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* X-ray evidence for the statistical disorientation of p-nitrochlorobenzene molecules in the crystal is contained in work ([7]).

corresponded to No. 1. It was assumed that in samples I–II No. 1 and partly I –II No. 2 the impurity content was about 50%.

The very first experiments on mixtures I and II showed that in samples I No. 1 and II No. 1 NQR lines of Cl^{35} appeared, narrower and moreover at a different frequency. The amplitudes of these narrow signals fell rapidly from sample to sample, so that in those parts of the zone-melted mixture where the impurity content was minimal (I No. 4 and II No. 4), the spectrum consisted only of a broad line corresponding to the disordered phase of n-$ClC_6H_4NO_2$.

The NQR spectrum of Cl^{35} of the control sample of zone-melted pure n-$ClC_6H_4NO_2$ contained the same broad line. Thus, it was possible to establish the fact of the formation of two crystalline modifications of n-chloronitrobenzene (see Table 1 and Fig. 1).

Table 1

NQR frequencies of Cl^{35}, spin-lattice relaxation times, and NQR line widths of Cl^{35} for n-$ClC_6H_4NO_2$ at 77° K

Phases of n-$ClC_6H_4NO_2$	ν, MHz	T_1, msec	$\Delta\nu$, kHz
Statistically disordered	34.88	350	350
In alloy with parabromonitrobenzene	35.421	400	10–20
In alloy with paraiodonitrobenzene	35.412	650	60–90

After a year, NQR of Cl^{35} was again investigated in the same samples. It then turned out that in the experiments with mixture I, during the elapsed time, in all samples I No. 1-4 there had been a complete phase transition to the ordered crystalline modification—the broad line was no longer observed. In the experiment with mixture II, the ordered phase was present in practically all samples II No. 1-4. However, in those samples where the impurity concentration was the smallest (II No. 4), the transformation over the elapsed period had not yet occurred completely. Consequently, one may suppose that this crystalline phase of n-$ClC_6H_4NO_2$ is less stable than I, but more stable than the disordered phase of pure parachloronitrobenzene. In control sample III of pure zone-melted n-$ClC_6H_4NO_2$, no changes occurred.

The course of orientation may be represented as follows: on the substrate crystals precipitating from the melt (which melt at a higher temperature), epitaxial growth of ordered n-chloronitrobenzene crystals takes place. At the same time, a considerable fraction of n-$ClC_6H_4NO_2$, i.e., crystals that have grown (precipitated) away from the centers of epitaxial growth (there is less substrate substance than the main substance, and the more so the more strongly the given sample has been purified by zone melting), remains in the former disordered modification. However, if the ordered phase at the same temperatures is more stable than the disordered one, then a slow phase transition must occur, with the initially formed crystals of the ordered phase acting as nuclei.

The conditions for the appearance and growth of epitaxial crystals are sufficiently complex and diverse. However, some of them are obvious: at least one of the lattice parameters of the corresponding crystals must have close values; the melting temperature of the "matrix"crystals must be higher than the melting temperature of the epitaxial crystals. Closeness of dimensions and similarity of molecular forms of both substances are desirable. For epitaxial ordered growth of crystals, the presence of sufficiently large dipole moments appears necessary both in the molecules of the "substrate" substance and in the molecules of the substance being oriented.

The formation or non-formation of a statistically disordered structure in substances analogous to n-chloronitrobenzene apparently depends on competition between packing factors and the tendency of the energy of dipole-dipole interaction toward a minimum. Of course, the manifestation of the effects of dipole-dipole interaction may be of substantial importance

only when the shapes and volumes of the "substituting" substituents are close to one another and when the molecules have large dipole moments [(2)].

Also of considerable interest is the character of the change in line widths in mixtures I and II. In case I the line widths of the ordered phase increase from 10 kc/s for I No. 1 to 20 kc/s for I No. 4, i.e., the line width decreases with increasing impurity concentration. This can apparently be explained by the fact that solid solutions of n-$BrC_6H_4NO_2$ in n-$ClC_6H_4NO_2$ in fact do not arise, and the defects formed (under interstitial dissolution) by the incorporated molecules

Fig. 1. NQR spectrum of Cl35 p-nitrochlorobenzene in an alloy with p-nitroiodobenzene (mixture II, 30% n-JC6H4NO2 + 70% n-ClC6H4NO2). a –disordered phase, b –new phase of p-nitrochlorobenzene

Figure 1: Fig. 1. NQR spectrum of Cl35 p-nitrochlorobenzene in an alloy with p-nitroiodobenzene (mixture II, 30% n-JC6H4NO2 + 70% n-ClC6H4NO2). a –disordered phase, b –new phase of p-nitrochlorobenzene

of n-$BrC_6H_4NO_2$ serve as sites of accumulation of the impurities present in the substance, promoting its additional purification. A "purification" of this kind of the substance was also observed by us earlier [11].

Fig. 1. NQR spectrum of Cl^{35} p-nitrochlorobenzene in an alloy with p-nitroiodobenzene (mixture II, 30% n-$JC_6H_4NO_2$ + 70% n-$ClC_6H_4NO_2$). *a* –disordered phase, *b* –new phase of n-nitrochlorobenzene.

The NQR signals of Br^{79} and J^{127} in mixtures I and II were not found (the standard method of signal detection was used [12]), since, evidently, solid solutions of n-$ClC_6H_4NO_2$ in n-$BrC_6H_4NO_2$ and in n-$JC_6H_4NO_2$ were formed. In samples II No. 1-4 the line widths of the oriented phase increased, following the rule usual for the formation of solid solutions: from II No. 4 to II No. 1, i.e., the greater the impurity concentration, the broader the line.

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Note: Figure translations are in progress. See original paper for figures.