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Abstract

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PHYSICS

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CHANGE IN THE INTENSITY OF NUCLEAR QUADRUPOLE RESONANCE IN A MOLECULAR CRYSTAL IRRADIATED WITH FAST ELECTRONS

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Nuclear quadrupole resonance ([1]) has proved to be a very sensitive means of studying a real crystal. The frequency at which resonance is observed depends on the magnitude of the gradient of the intracrystalline electric field q in which the nucleus is located, while the width of the resonance line is determined by the spread of values of q from nucleus to nucleus. Therefore an imperfection of the crystal lattice directly and strongly affects the quadrupole-resonance signal. Thus the quadrupole-resonance line of the isotope Cl^{35} in n-dichlorobenzene has a width of 1.5 kHz at a frequency of 34.29 MHz. If the value of q acting on some Cl^{35} nucleus changes so much that the resonance frequency for this nucleus is shifted by 2–3 kHz, it will cease to contribute to the observed part of the absorption line. The height of the quadrupole-resonance signal will then decrease. Such a frequency shift requires only about 10 ergs of energy per mole of nuclei affected by the perturbing action (i.e., $\sim 10^{-10}$ kcal/mole). Such high sensitivity to small effects leads, for example, to the fact that the introduction of a 1–2% impurity into the lattice of the crystal under study reduces the intensity of quadrupole absorption by a factor of 10 or more ([2]).

We used nuclear quadrupole resonance as an indicator of radiation damage in polycrystalline samples of n-dichlorobenzene subjected to various doses of irradiation with electrons of energy 750 keV.

The resonance was observed with a frequency-modulated quadrupole radiospectrometer with synchronous detection and recording of the signal on a self-recording millivoltmeter ([3]). In contrast to the instrument described earlier, a superregenerative generator-detector with a diode detector in the cathode circuit was used (Fig. 1). The voltage on the generator circuit was continuously monitored. The quadrupole-resonance line from each sample was recorded many

Fig. 1. Generator-detector

Figure 1: Fig. 1. Generator-detector

times. Each point on the graph (Fig. 2) is the result of processing such a series of lines. The error in this procedure does not exceed 5%. Samples of equal weight (4.1 g) were used.

In considering Fig. 2, two circumstances are noteworthy: (1) the presence of a "saturation" region, when an increase in the irradiation dose ceases to have a noticeable effect on the intensity of the quadrupole-resonance signal; (2) this region corresponds to an unexpectedly small decrease in the signal intensity compared with the signal intensity of the unirradiated sample ($A/A_0 = 0.75$). A substantial decrease in the signal (down to $A/A_0 = 0.3$) was observed in a sample that was insufficiently cooled during irradiation, as a result of which melting centers formed in it. In this case, despite the loss by the sample overheated during irradiation of both its external similarity to unirradiated crystals of *n*-dichlorobenzene and its melting point (in attempts to determine the melting point, a resinous mixture of complex composition was obtained), the frequency of the nuclear quadrupole resonance

remained exactly the same. This was shown by placing equal amounts of irradiated and unirradiated crystals in the spectrometer coil. We note that an analogous saturation of radiation damage, recorded by means of quadrupole resonance, was observed in [4], where hard γ-radiation from Co^{60} was used. There this phenomenon was not explained.

These facts find a simple explanation if one assumes that chemical transformations under the action of γ- and β-radiation, leading to a shift of the quadrupole-resonance frequency, can proceed irreversibly only at those sites of the crystal where the packing density is reduced in comparison with the ideal lattice (block boundaries and similar defects). At sites with normal packing, the arrangement of the fragments of the molecule formed upon rupture of a chemical bond remains rigidly fixed, and the bond is restored instantaneously.

Fig. 1. Generator-detector

As the voids become filled with fragments of molecules knocked out from the surfaces of the blocks, the mobility of fragments cleaved off later will decrease substantially, which will correspondingly reduce the probability of irreversible bond rupture. To confirm the possibility of such "locking" of chemical transformations in a thin layer on the surface of a block, it is sufficient to assume that the products of these transformations are packed in the voids more loosely than the original molecules are packed in the blocks. The volume of these products themselves, as shown by calculations carried out for tentative schemes of chemical transformations of *p*-dichlorobenzene, agrees to within 2–3% with the volume of the original molecules.

The thickness of the layer on the surface of a block that will be destroyed before further chemical transformations become "locked" depends on the width of the gap between blocks. Between these quantities there is the simple relation

$$b = 2na_0\left(\frac{k_0}{k} - 1\right), \tag{1}$$

where b is the width of the gap between blocks; a_0 is the average size of a molecule; n is the number of monomolecular layers on the surface of a block that will be destroyed by the moment of "locking" ; k_0 is the packing density of molecules in the block, and k is the packing density of the molecular "fragments" in the voids. Let us use the value typical of organic crystals, $k_0/k = 1.25$. Then it follows from (1) that destruction of the block surface by radiation ceases after decomposition of the molecules in a layer whose thickness is twice the width of the gap between blocks. In (1) no account is taken of the possible escape from the specimen of gaseous radiolysis products. Taking this circumstance into account would lead to a further decrease in the value of b necessary for accommodating the "fragments."

Thus, after the destruction of molecules in a thin layer on the surfaces of blocks, crack boundaries, etc., a further increase in the irradiation dose will not affect the magnitude of the quadrupole-resonance signal: a boundary is stabilized between the correctly packed region, where irradiation cannot cause chemical transformations, and the region in which any changes no longer affect quadrupole absorption, since the Cl^{35} nuclei present there had already earlier ceased to make an appreciable contribution to the resonance line. The decrease in the value of A/A_0 upon heating the specim-

This is easily explained by the fact that the presence of melting centers increases the number of poorly packed and completely liberated molecules.

From this point of view, the relative decrease in the height of the quadrupole-resonance signal in the irradiated sample must be equal to the ratio of the number of molecules N_1 located in sites with loosened packing to the number of normally packed molecules N:

$$\frac{A_0 - A}{A} = \frac{N_1}{N}. \tag{2}$$

If measures are taken to eliminate local overheatings, the experiment gives the ratio N_1/N in the unirradiated sample at the irradiation temperature. The ratio N_1/N can readily be compared with the block structure of the crystal. If the surface of the blocks is responsible for the decrease in the quadrupole-resonance signal in the irradiated crystal, then $N_1/N = V_1/V$, where V is the mean volume of a block and V_1 is the volume of its surface layer destroyed by the radiation. Let Δa be the thickness of this surface layer and a the linear size of the block. Then $V_1 = 6a^2 \cdot \Delta a$, $V = a^3$, and, taking (2) into account,

Fig. 2. Decrease in the amplitude of the quadrupole-resonance signal as a function of the increase in the absorbed irradiation dose. Electron energy 750 keV. The dose unit corresponds approximately to 10^8 rad.

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$$\frac{\Delta a}{a} = \frac{1}{6} \cdot \frac{A_0 - A}{A_0}. \tag{3}$$

Fig. 2. Decrease in the amplitude of the quadrupole-resonance signal as a function of the increase in the absorbed irradiation dose. Electron energy 750 keV. The dose unit corresponds approximately to 10^8 rad.

For simplicity it has been assumed that the block has the form of a cube. We obtain a minimum estimate of the block dimensions by assuming that $\Delta a = a_0$, i.e., that a monomolecular layer on its surface is destroyed by the radiation. For an *n*-dichlorobenzene molecule $a_0 \simeq 8$ Å; hence, on the basis of the experimental value of A/A_0 and equation (3), we obtain $V = 7 \cdot 10^6$ Å^3. Since the volume of the unit cell of *n*-dichlorobenzene is 350 Å^3, such a block contains $4 \cdot 10^4$ molecules. If $\Delta a = 3a_0$, then the block will contain $\sim 10^6$ molecules. Thus, an estimate of the block dimensions on the basis of the assumption developed here gives reasonable orders of magnitude. It is also interesting that the joint consideration of equations (1) and (3), taking into account the experimental value

$$\frac{A_0 - A}{A_0} = 0.25$$

(at $k_0/k = 1.25$), leads to the conclusion that voids, cracks, etc., occupy slightly more than 4% of the crystal volume, which agrees well with data obtained by X-ray structural analysis.

It follows from the above that a carefully grown single-crystalline sample, in which the lattice is close to ideal, should possess considerably greater resistance to ionizing γ- and β-radiation than a polycrystalline one. We propose to test this by means of the same method.

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