
**DEFECTS, DISLOCATIONS,
AND PHYSICS OF STRENGTH**

Mixed Crystals of *p*-Dichlorobenzene with *p*-Bromchlorobenzene in the Presence of Vacancies in the Structure

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Abstract—Polarization studies of low-frequency Raman spectra of solid solutions of *p*-dichlorobenzene with *p*-bromchlorobenzene (50% *p*-dichlorobenzene) were carried out. Analysis of the lattice vibration spectra of these mixed crystals shows that vacancies can be present in their structure. The presence of vacancies is responsible for the emergence of additional lines, including those in the 70 cm⁻¹ region. The calculation of the diffusion activation energy in a mixed crystal proves that its magnitude is determined by the spatial arrangement of *p*-bromchlorobenzene molecules in the lattice, their orientation relative to parahalides, and (to a lesser extent) temperature variations. © 2000 MAIK “Nauka/Interperiodica”.

The application of low-symmetry organic crystals in molecular electronics has increased significantly. These materials are promising in information recording and data processing [1]. The crystals for practical applications may contain defects such as vacancies. The presence of vacancies in a crystal leads to diffusion impeding a decrease in the area of information recording [2]. The diffusion rate depends on the temperature variation as well as on the impurity distribution in the crystal (for mixed crystals).

The presence of vacancies in a crystal can be determined with the help of low-frequency Raman scattering, since their presence affects lattice vibrations and is manifested in the spectra. An analysis of spectra for mixed crystals consisting of centrosymmetric molecules (*p*-dichlorobenzene with *p*-dibromobenzene) reveals additional low-intensity lines whose emergence is associated with a disorder in the distribution of impurity molecules and the presence of vacancies [3]. Besides, the activation energy in these mixed crystals depends on the temperature variation and on the crystallographic direction to a lesser extent than in the component crystals.

It would be interesting to find out whether this dependence is preserved for solid solutions in which noncentrosymmetric molecules constitute one of the components.

For our experiments, we chose isomorphous crystals of *p*-dichlorobenzene (α modification) and *p*-bromchlorobenzene forming solid solutions for any concentration.

According to the x-ray diffraction data [4] and NQR data [5], noncentrosymmetric molecules of *p*-bromchlorobenzene, as well as *p*-dichlorobenzene (α modification), are crystallized in the centrosymmetric space group $P2_1/a$ with two molecules in a unit cell

owing to statistically disordered distribution of molecules relative to parahalides. The spectra of lattice vibrations for such crystals must contain six high-intensity lines associated with orientational vibrations and three lines associated with translational vibrations.

Figure 1a shows the lattice vibration spectrum (the xz component of the scattering tensor) for a mixed crystal of *p*-dichlorobenzene with *p*-bromchlorobenzene with 50% of *p*-dichlorobenzene.

The experimental spectrum contains six high-intensity lines three of which are of the B_g type (25.1, 44.4, and 100.7 cm⁻¹) and the remaining three, of the A_g type (45.4, 50.1, and 92.5 cm⁻¹) as well as a series of low-intensity lines (19.5, 29.5, 38.4, 62.2, 72.3, and 83.0 cm⁻¹).

In order to interpret the experimental spectra, we calculated the lattice vibration spectrum for a mixed crystal of *p*-dichlorobenzene with *p*-bromchlorobenzene (50% *p*-dichlorobenzene). It was assumed that the *p*-bromchlorobenzene molecules in the structure of the mixed crystal are distributed at random relative to parahalides as in pure *p*-bromchlorobenzene.

The molecular structure was assumed to be perfectly rigid. The interaction between the molecules was described by the atom–atom potentials method [6]. The coefficients in the interaction potential were the same as in analysis of the frequency spectra of *p*-dichlorobenzene and *p*-dibromobenzene [3]. The spectra of disordered crystals were calculated by Dean’s method [7], which allows one to determine the eigenvalues for high-order matrices. The results of calculations were used to plot histograms that indicate the probability of the emergence of spectral lines in the chosen frequency range.

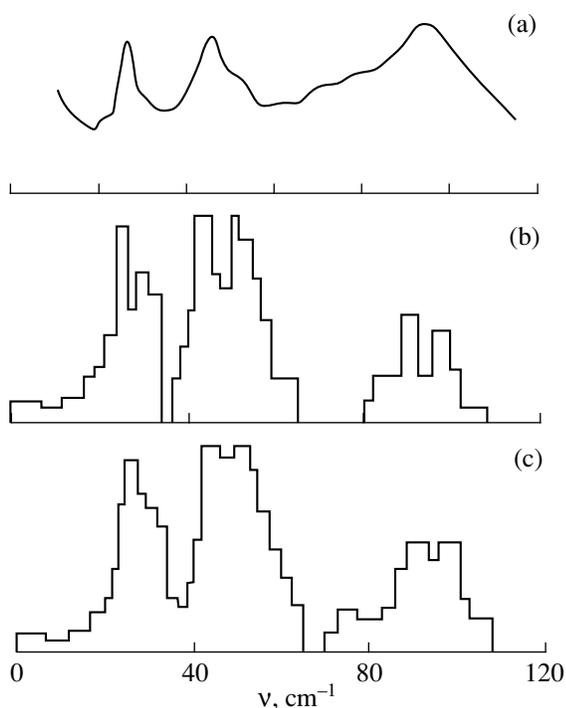


Fig. 1. Experimental low-frequency spectrum for a mixed crystal of *p*-dichlorobenzene with *p*-bromchlorobenzene containing 50% *p*-dichlorobenzene [(a) the *xz* component of the scattering tensor] and histograms obtained from calculations (b) in the presence of vacancies in the structure and (c) in the absence of vacancies.

Figures 1b and 1c show the histogram of the frequency spectrum of lattice vibrations for a mixed crystal without vacancies and in the presence of vacancies, respectively. In the latter case, additional lines emerge in the region of 70 cm^{-1} , which agrees with the experimental data.

Values of the energies E_L , E_r , E_f , E_m , and E_d (kcal/mol) at 100 and 300 K

	5% <i>p</i> -dichlorobenzene and 95% <i>p</i> -bromchlorobenzene		95% <i>p</i> -dichlorobenzene and 5% <i>p</i> -bromchlorobenzene	
	300	100	300	100
E_L	15.55	17.0	16.4	17.43
E_r	0.55	0.56	0.58	0.68
E_f	15.0	16.44	15.82	16.75
$E_m^{[001]}$	4.0	4.2	4.8	4.9
$E_d^{[001]}$	19.0	20.64	20.62	21.65
$E_m^{[010]}$	3.3	3.4	3.1	3.3
$E_d^{[010]}$	18.3	19.84	18.92	20.05

An analysis of eigenvectors revealed that all vibrations are mixed with dominating translational or orientational vibrations. It was found that the lines in the vicinity of 29.5 , 38.4 , and 62.2 cm^{-1} are associated predominantly with translational vibrations. This agrees with the IR absorption data for *p*-bromchlorobenzene (26.0 , 32.0 , and 54.0 cm^{-1}) [8]. Therefore, the emergence of extra lines in the region of 70 cm^{-1} is due to the presence of vacancies.

We calculated the energies of the lattice, of vacancy formation, and of migration of molecules of mixed crystals of *p*-dichlorobenzene with *p*-bromchlorobenzene at 300 and 100 K. The analysis was carried out for two cases of low impurity concentrations. In the first case, 5% of *p*-bromchlorobenzene were added to the lattice of *p*-dichlorobenzene, and second, 5% of *p*-dichlorobenzene were added to the lattice of *p*-bromchlorobenzene.

The table contains the calculated values of lattice energy (E_L) for a mixed crystal without vacancies at 300 and 100 K for the two cases of component concentrations.

In order to determine the arrangement of molecules in the lattice of a mixed crystal with vacancies, the free energy was minimized in the orientations and displacements of the centers of mass of the molecules under investigation. In view of relaxation, the energy of the mixed crystal changed by E_r . The table also contains the calculated value of the energy of vacancy formation E_f .

In an analysis of the energy of migration, a molecule was displaced step by step from the position $(0, 0, 0)$ along a chosen direction towards a vacancy. The length of a step was 0.2 \AA . After each step, the crystal energy was minimized in accordance with the above-described procedure. The results of calculations are presented in Fig. 2 and in the table, where $E_m^{[001]}$ is the energy for migration of an impurity molecule along the crystallographic direction $[001]$ and $E_m^{[010]}$ is the same along the direction $[010]$. The calculated values of the activation energy E_d are also presented in the table. The activation energy increases upon cooling, which is manifested in a change in the diffusion rate. The energy for migration changes insignificantly in this case. This is also observed for mixed crystals consisting of centrosymmetric molecules (*p*-dibromobenzene with *p*-dichlorobenzene) [3].

The curves in Fig. 2 show the variation of the potential energy upon a displacement of an impurity molecule in the lattice of a mixed crystal of *p*-dichlorobenzene with *p*-bromchlorobenzene along the crystallographic directions $[001]$ (Fig. 2a) and $[010]$ (Fig. 2b).

Curves 1 in Fig. 2 correspond to the concentration of a mixed crystal (5% of *p*-dichlorobenzene and 95% of *p*-bromchlorobenzene), while curves 2 correspond to

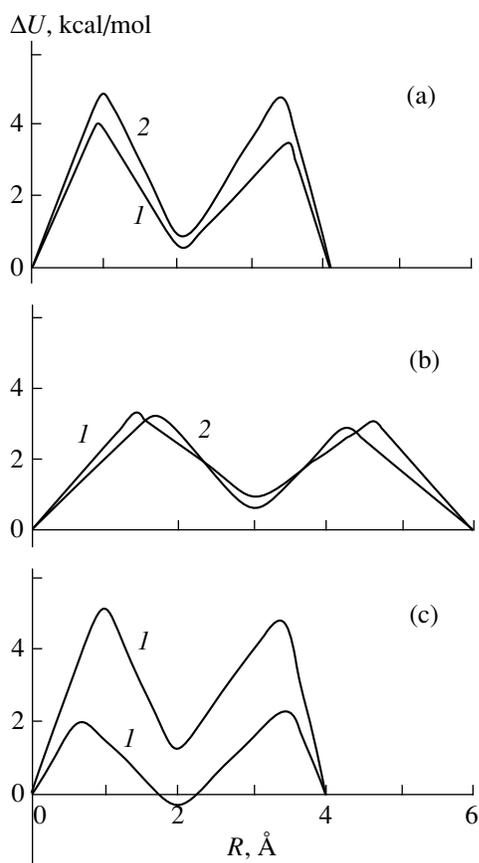


Fig. 2. Variation of potential energy upon the displacement of a migrating molecule towards a vacancy in crystallographic directions (a) [001] and (b) [010]. (c) Energy variation for various distributions of *p*-bromchlorobenzene molecules over *p*-positions.

the 5% *p*-bromchlorobenzene and 95% *p*-dichlorobenzene concentrations of the components.

In view of the disordered arrangement of *p*-bromchlorobenzene molecules in the lattice of the mixed crystal, the environment of a migrating molecule is different at different points of the crystal, which is manifested in the energy for migration. By way of an example, Fig. 2c graphically shows the potential energy variation upon a displacement of a *p*-dichlorobenzene molecule in the mixed crystal (with 95% of *p*-bromchlorobenzene) for a uniform distribution of molecules over the crystal volume, but for different orientations of *p*-bromchlorobenzene molecules relative to parahalides.

It can be seen from the figures that the energy for migration can vary over a wide range. This distin-

guishes mixed crystals formed by noncentrosymmetric molecules from those composed of centrosymmetric molecules, in which the variation of the energy for migration from cell to cell depends only on the distribution of impurity molecules over the crystal volume.

While comparing the experimental results on the activation energy of mixed crystal with the calculated values, one must apparently consider the averaged energy values along the chosen direction. However, we are not aware of any experimental results on the diffusion activation energy in mixed crystals of *p*-dichlorobenzene with *p*-bromchlorobenzene.

Thus, we have proved that the structure of mixed crystals of *p*-dichlorobenzene with *p*-bromchlorobenzene contains vacancies. Their presence is manifested in the emergence of extra spectral lines in the vicinity of 70 cm^{-1} . The analysis of migration energy in these mixed crystals reveals that its magnitude depends not only on the spatial distribution of an impurity over the crystal volume, but also on the arrangement of *p*-bromchlorobenzene molecules relative to parahalides. For a certain distribution of molecules in the structure of the crystal consisting of a mixture of noncentrosymmetric and centrosymmetric molecules, the variation of the migration energy with temperature is insignificant; this is also observed for mixed crystals consisting of centrosymmetric molecules.

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