Intermolecular interaction in a benzene crystal at high pressure

S. I. Gaĭdaĭ and K. P. Meletov

Institute of Solid State Physics, USSR Academy of Sciences

(Submitted 19 April 1991)
Zh. Eksp. Teor. Fiz. **100**, 1567–1576 (November 1991)

The absorption spectra for crystal benzene in the excitonic transition $A_{1g} \to B_{2u}$ region at $T = 4.2$ K and pressure to 4 GPa are measured. For pressure 2.35 GPa, the monotonous red shift and increase of the factor-group splitting of exciton bands are found to have a jump-like change, what is due to the orthorhombic to monoclinic structure transition. The dependence of the factor-group splitting and excitonic band shift upon the crystal density in both phases is found. The intermolecular coupling is shown to be short-range and cannot be described adequately by the multipole expansion approximation within the Coulomb interaction. The results obtained indicate the important role of the electron exchange coupling due to overlapping the electron orbitals of coupling molecules.

1. INTRODUCTION

Research into the properties of crystalline benzene under high pressure has recently resumed. Raman and infrared spectroscopy and x-ray diffraction have been used to investigate the phonon spectra and the crystal structure of benzene at pressures up to 30 GPa.[1-3] The results have revealed new high-pressure phases and yielded the dependence of the crystal-structure parameters on the pressure in the range up to 20 GPa. The results provide a basis for the investigation of the intermolecular interaction in strongly compressed crystalline benzene. Research of this type was carried out in the recent past on anthracene and naphthalene molecular crystals under high hydrostatic pressure.[4,5] A distinguishing feature of molecular crystals is that intermolecular interaction is considerably weaker than intramolecular, and the molecules preserve their individuality in the crystal. Molecular interaction determines nevertheless the characteristic differences between the energy spectrum of the crystal and the free-molecule spectrum, viz., static displacements of the electron terms and their splitting into a quasicontinuous excited-state spectrum. The evolution of the energy spectrum of molecular crystals at high pressures makes it possible to determine the characteristic features of the intermolecular interactions in the crystal.

It should be noted that the cause of the interest in this question is that whereas theoretical calculation methods based on various approximations yield satisfactory results for the strength of this interaction at normal pressure, they cannot describe well enough its pressure dependence. In particular, the experimental pressure dependences of the static displacement and the group-expansion factor of the exciton bands, obtained for anthracene and naphthalene crystals, do not agree with the dipole approximation for intermolecular interaction, and attempts of adequately describing this interaction by using other interaction models has so far not yielded a satisfactory result.[6-8] It is therefore vital to extend the experimental investigations of this type to include molecular crystals having different molecule sizes as well as different exciton-transition dipole moments, which determine the distances between molecules as well as the energy of the intermolecular interaction.

We have measured the absorption spectra of crystalline benzene in the region of the lowest singlet exciton transition $A_{1g} \to B_{2u}$ at $T = 4.2$ K and at pressures up to 4 GPa. We have observed that when the pressure is increased the monotonic red shift and the increase of the group-splitting of the exciton band give way to a jumplike shift and to an increase of the splitting at the phase transition from the orthorhombic to the monoclinic phase at $p = 2.35$ GPa. Further increase of the pressure in the monoclinic phase is also accompanied by a monotonic red shift and by an increase of the group splitting factor of the exciton bands. These measurements yielded the dependence of the static displacement and of the factor-group splitting of the exciton bands on the crystal density in both crystalline phases, and show that the intermolecular interaction is short-range. Just as in the case of anthracene and naphthalene crystals, it is not satisfactorily described in the approximation of pure Coulomb interaction, and to describe it adequately it is apparently necessary to take into account the electronic exchange interaction due to overlap of the electron orbitals of neighboring molecules.

2. EXPERIMENT

Measurements at high pressure were made using sapphire anvils, which permitted the spectral range to be extended to the far ultraviolet where the crystalline-benzene exciton-absorption region is located. The pressure was produced in the working volume of a chamber, constituting an opening of 300 μm diameter in a copper-foil liner 20–50 μm thick. The pressure was determined, accurate to 0.05 GPa, from the displacement of the ruby R_1 luminescence line at room and helium temperatures (Refs. 9 and 10). The benzene single crystals were grown in the working volume of the chamber from a 20:4:1 benzene:methanol:ethanol mixture which solidified after slight compression. Heating the chamber to the melting temperature yielded a single seed, from which the single crystal was grown by slow cooling. The high-grade grown crystals were hexagonal slabs 10–30 μm thick, had a characteristic transverse dimension 250 μm, and were placed in an alcohol mixture that ensured hydrostatic compression conditions up to 10 GPa. The benzene-crystal absorption spectra were measured at liquid-helium temperature for two incident-light polarization directions by a procedure previously described.[11] The spectral resolution of the instrument was approximately 5 cm^{-1}, and the

0038-5646/91/110867-05$03.00

intensity, with allowance for the depolarization of the light, was determined at an approximate accuracy 10%.

3. EXPERIMENTAL RESULTS

Figure 1 shows the absorption spectra of crystalline benzene for $T = 4.2$ K and for different pressures in the region of the lowest singlet exciton transition $A_{1g} \rightarrow B_{2u}$. This transition is symmetry-forbidden in a free molecule but in a crystal the mutual polarization of the molecules alters the symmetry of the π-electron cloud and symmetry-forbidden transitions, $A_{1g} \rightarrow B_{2u}$ are allowed in the spectrum. It should be noted that the molecular transition $A_{1g} \rightarrow B_{2u}$ is transformed in a benzene crystal with orthorhombic symmetry and with four molecules per unit cell into a quasicontinuous exciton spectrum consisting of four branches. At the point $\mathbf{k} = 0$ these branches correspond to four excitonic states with symmetries B_{1u}, B_{2u}, B_{3u}, and A_u. Optical transitions are allowed for the first three states, and the transition to the state A_u is symmetry-forbidden.[12]

The upper spectrum of Fig. 1 corresponds to 0.25 GPa and is practically the same as the spectrum at normal pressure. It starts out from narrow exciton-absorption lines: the first line corresponds to a transition to an exciton state with symmetry B_{1u} and frequency $\omega_A = 37\,803$ cm^{-1}, and is polarized parallel to the **a** axis of the crystal. The second line corresponds to a transition into an exciton state of symmetry B_{3u} and frequency $\omega_c = 37\,842$ cm^{-1} and is polarized parallel to the **c** axis of the crystal. The transition into a state of symmetry B_{2u} corresponds to an exciton line of frequency $\omega_B = 37\,848$ cm^{-1} polarized parallel to the **b** axis of the crystal. It is not shown in the spectra of Fig. 1, since it is suppressed by neighboring stronger C-exciton line. The wide structureless phonon wing behind the C-exciton line is due to exciton–phonon transitions with generation of lattice phonons. On the violet edge of the spectrum is located a total-absorption region corresponding to the so-called M band—a vibronic transition with participation of a non-fully-symmetric intramolecular oscillation E_{2g}. The dashed and solid lines of Fig. 1 show the absorption spectra for two light-polarization directions. They differ only in intensity, since the orientation of the developed crystal plane does not agree with the orientations of **ab**, **ac** and **bc** planes.

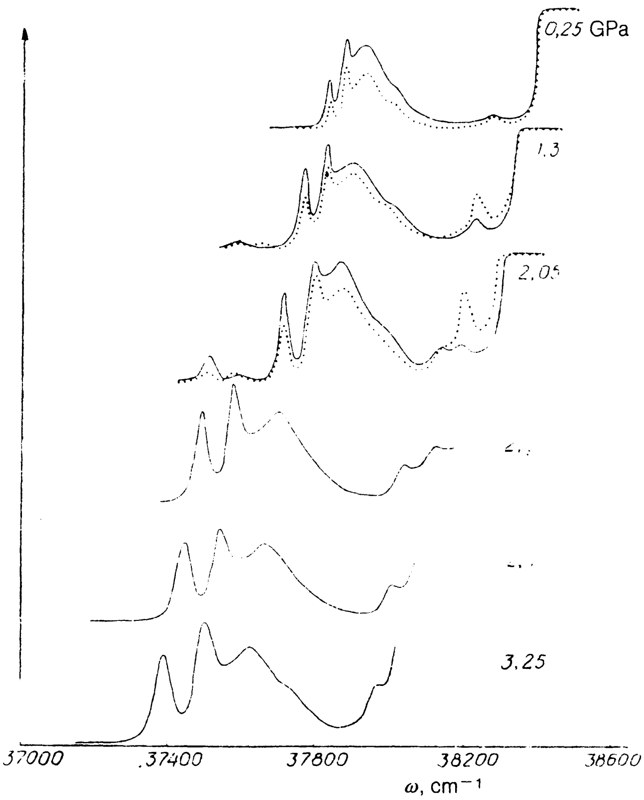

FIG. 1. Crystalline-benzene absorption spectra at $T = 4.2$ K and pressures up to 3.25 GPa in the region of the $A_{1g} \rightarrow B_{2u}$ exciton transition. The solid and dashed lines show the spectra for different directions of the light polarization.

All the lines are shifted towards the red side of the spectrum with increase of pressure, while the factor-group splitting of the excitonic bands and their intensity in both polarizations increase monotonically. The main feature of the spectrum remain unchanged up to 1.3 GPa pressure, at which a weak absorption band appears on the red edge of the spectrum, at an approximate distance 160 cm^{-1} from the A-exciton band. This band has a doublet structure: in one of them the intensity polarizations of the components are approximately equal, and in the other the red component is significantly stronger. The splitting of this band grows rapidly with increase of pressure, to approximately 70 cm^{-1} at $p = 2.05$ GPa, exceeding the factor-group splitting of the A and C exciton bands at this pressure. The absorption spectrum changes radically at 2.35 GPa: The A- and C-exciton bands execute a 160 cm^{-1} jump towards the red side, to the location of the previously produced new absorption bands, and the factor-group splitting jumps from 64 to 85 cm^{-1}. Further increase of the pressure is again accompanied by a monotonic displacement and by an increase of the splitting of the bands.

The jumplike change of the spectrum is due to a phase transition from the orthorhombic structure P_{bca} with four molecules per unit cell to a monoclinic with two molecules per unit cell. This transition was observed earlier in measurements of the pressure dependence of the microscopic volume of the crystal and in a differential thermal analysis.[13,14] It was investigated in detail by x-ray diffraction: the parameters of the new structure were determined and it was shown that the volume changes in the transition by 1.5%.

The small change of the crystal volume in the phase transition is the cause of the existence of a rather broad two-phase region: the weak absorption bands on the red edge of the spectrum correspond to seeds of a new monoclinic phase. They always occur at an approximate pressure 1.3 GPa, but in some cases no phase transition occurs in the bulk of the crystal below 3.3 GPa. These results are illustrated in Fig. 2, which shows the dependences of the A and C excitonic bands on the pressure. The pressure dependences of the absorption of the A and C excitonic bands in the orthorhombic phase are shown by the light rectangles and circles in the figure, and in the monoclinic phase by dark rectangles and circles. The light rectangles and circles with center dots correspond to the positions of the A and C exciton bands for the seeds of the monoclinic phase in a two-phase sample. The average rates of the band displacements in the orthorhombic phase are 61 and 47 cm^{-1}/GPa for the A and C excitons, respectively, and the factor-group splitting increases from an initial value 40 cm^{-1} at a rate of 14 cm^{-1}/GPa. In the monoclinic phase, the average displacement rate for the A and C excitons is 91 and 70 cm^{-1}/GPa, and the factor-group splitting

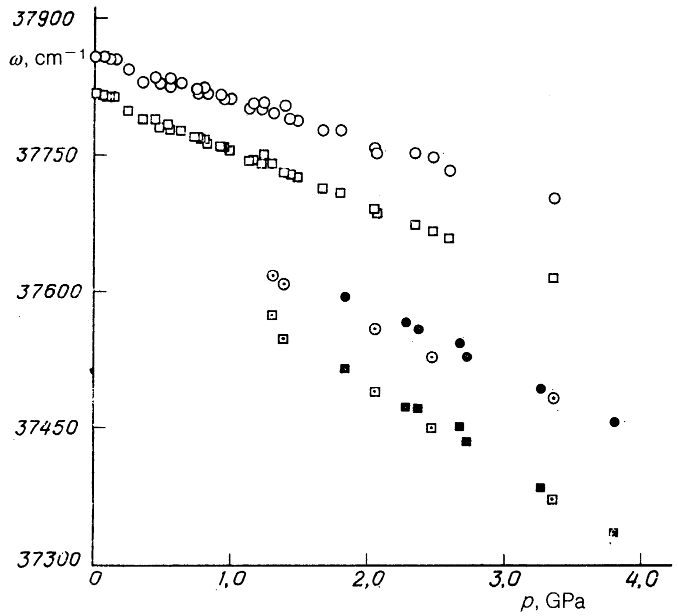

FIG. 2. Pressure dependence of the location of crystalline-benzene exciton absorption spectra. Light rectangles and circles—*A*- and *C*-exciton bands in orthorhombic phase; dark rectangles and circles—the same in monoclinic phase; rectangles and circles with center dots—the same for seeds of the monoclinic phase in a two-phase sample.

increases from an initial value 74 cm^{-1} at 1.4 GPa at an average rate of 21 cm^{-1}/GPa.

As seen from the figure, the total displacement of the exciton bands prior to the transition to the orthorhombic phase is approximately one-third the jumplike displacement in the transition to the monoclinic phase. Since the volume is decreased much less by the phase transition than by compression of the crystal to 1.4 GPa, the jumplike displacement cannot be attributed only to a decrease of the distance between the molecules. It can be due to a change of the molecule orientations in the phase transition, which should also enhance the intermolecular interaction. It should be noted that the possibility of a phase transition due to a change of the molecule orientation was pointed out by Broude[12] in an analysis of the absorption spectra of crystalline benzene. The plane of the benzene molecule in the orthorhombic structure is inclined 12° to **b** axis of this crystal: if this angle is made equal to zero, the structure becomes monoclinic with two molecules per unit cell, and the period along the **b** axis of the crystal is halved. X-ray-diffraction measurements point indeed to a decrease of this period by a factor of two,[2] attesting apparently to a change of the orientation of the molecules.

Thus, the experimental results on the displacement and factor-group splitting of exciton bands contains important information on the intermolecular interactions in the two crystal phases of the benzene. This information will be analyzed in the next part of the paper.

4. DISCUSSION OF RESULTS

According to molecular-exciton theory[15] the static displacement *D*, equal to the difference between the energies of the electron transition in a free molecule and the unsplit molecular term in the crystal, is defined as

$$D=\sum_{\mathbf{n}\alpha}{}'\Big[\int|\varphi_{\mathbf{m}\beta}{}^{f}|^{2}\,V_{\mathbf{n}\alpha\mathbf{m}\beta}\,|\varphi_{\mathbf{n}\alpha}{}^{0}|^{2}\,d\tau-\int|\varphi_{\mathbf{m}\beta}{}^{0}|^{2}\,V_{\mathbf{n}\alpha\mathbf{m}\beta}\,|\varphi_{\mathbf{n}\alpha}{}^{0}|^{2}\,d\tau\Big].$$

The summation here is over all the crystal molecules, the subscripts label different translationally nonequivalent molecules, **n** denotes the radius vectors of the different cell, $V_{\mathbf{n}\alpha\mathbf{m}\beta}$ is the operator of the interaction energy of the molecules $\mathbf{n}\alpha$ and $\mathbf{m}\beta$, $\varphi_{\mathbf{m}\beta}$ is the wave function of the molecule $\mathbf{m}\beta$, and the subscripts *f* and 0 label the excited and ground states of the molecule.

The factor-group splitting of the exciton bands is determined by the elements of the resonant-interaction matrix

$$L_{\alpha\beta}{}^{f}(\mathbf{k})=\sum_{\mathbf{n}}{}'\,M_{0\beta\mathbf{n}\alpha}\exp(i\mathbf{kn}),\qquad(2)$$

where

$$M^{f}_{0\beta\mathbf{n}\alpha}=\int\varphi_{\mathbf{n}\alpha}{}^{*0}\,\varphi_{0\beta}{}^{*f}\,V_{\mathbf{n}\alpha0\beta}\,\varphi_{0\beta}{}^{0}\,\varphi_{\mathbf{n}\alpha}{}^{f}\,d\tau\qquad(3)$$

are the matrix elements of the transfer of the excitation *f* from the $\mathbf{n}\alpha$ to the $\mathbf{m}\beta$ molecule.

It is customary to take into account in the calculation of the excitation-transfer energy matrix elements only the Coulomb interaction in the dipole approximation. In the case of the benzene crystal, the first nonvanishing term of the expansion of the molecule-molecule interaction, in terms of the multipoles in the Heitler–London approximation, is the octupole–octupole interaction term.[16] In this case its value decreases with increase of the intermolecular distance *R*, in proportion to R^{-7}, and only the interaction between nearest neighbors is usually taken into account in the sum of (2). The static displacement *D* is determined by difference between the energies of the Van der Waals interaction of the molecule with all the surrounding crystal molecules as the molecule becomes excited, and decreases in this approximation in proportion to R^{-6}.

The experimental data on the displacement and the factor-group splitting of the exciton bands in the crystal phases of benzene allows us to determine the dependences of these quantities on the intermolecular distance. Strictly speaking, one can determine their exact dependence on the crystal volume, since we have experimental data on the pressure dependence of the crystal volume.[2] These dependences are fully equivalent if the compression of the crystal causes a proportional decrease of the crystal-structure parameters. It follows from x-ray diffraction measurements that there is no such proportionality in both crystalline phases of benzene. This means, in particular, that the dependence of the pair-interaction energy on the mutual distances, for molecule pairs located on different crystallographic directions, may differ somewhat.

Recognizing, however, that the static displacement and the factor-group splitting are determined by the joint contribution of pair interactions of different molecule pairs, one can hope that the summation will average somewhat this dependence, and the experimentally determined exact dependence on the volume reflects the dependence on the intermolecular distances. It must also be remembered that the structural data for the benzene crystal at high pressure were obtained at room temperature, whereas the optical absorption spectra were measured at liquid-helium temperature. Taken by itself, the cooling of the crystalline benzene to liquid-helium temperature at normal pressure decreases its volume by 10%, since the benzene crystallization point (278 K) is close to room temperature. This is the cause of the high compressibility of crystalline benzene in the initial pressure region: when compressed to 1 GPa, its volume decreases by 12.8%, but with further compression from 1 to 2 GPa its volume decreases only by 5.3%.[2] Cooling the benzene to liquid-helium temperature causes the same decrease of its volume as its compression at room temperature to approximately 0.7 GPa.

This circumstance can be used to determine the relative change of the benzene crystal volume in the orthorhombic phase at liquid-helium temperature; since its volume at normal pressure and at $T = 4.2$ K is equal to the volume at room temperature and 0.7 GPa pressure, the other values of the volume at $T = 1.2$ K correspond to volumes at room temperature displacemented by 0.7 GPa. It is difficult to estimate the error of such an approximation, but it is clear that it decreases with increase of pressure, for in this case the data on the compressibility at room and helium temperatures approach each other. It should be stated that for the monoclinic phase of benzene we used directly the room-temperature data, for lack of data on the temperature expansion.

Figure 3 shows in log-log scale the reduced dependence of the relative change S_p/S_0 of the factor-group splitting of the A and C exciton bands on the relative density change P_p/P_0 in the orthorhombic phase of the benzene crystal. It includes the orthorhombic-phase data obtained for a two-phase sample. Estimates show that the volume of the monoclinic phase in such a sample does not exceed 10% for a maximum pressure 3.3 GPa, at which the crystal density increases by 17%. Data on the factor-group splitting are described by the power-law dependence $S_p/S_0 \propto (P_p/P_0)^{5.5 \pm 0.2}$, shown by a solid line in Fig. 3, while the dotted line corresponds to the dependence $S_p/S_0 \propto (R_0/R_p)^7 = (P_p/P_0)^{2.33}$, which describes the octupole-octupole approximation of the resonant interaction.

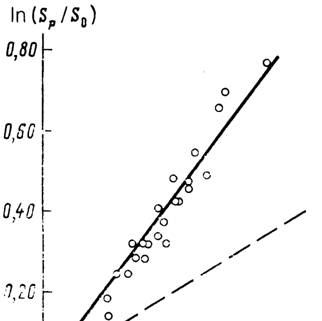

FIG. 3. Exciton-band factor-group splitting $\ln(S_p/S_0)$ vs the relative density change $\ln(P_p/P_0)$ in the orthorhombic phase of a benzene crystal. Solid line—approximation with a power-law dependence $S_p/S_0 \propto (P_p/P)^{5.5 \pm 0.2}$, dashed line—octupole-octupole approximation $S_p/S_0 \propto (P_p/P_0)^{2.3}$.

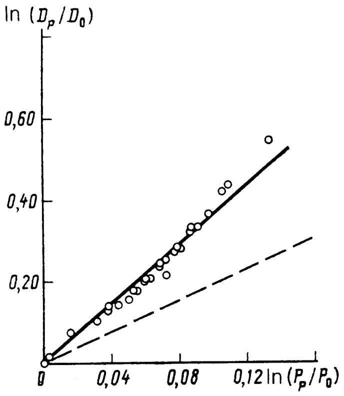

FIG. 4. Dependence of the static displacement of the exciton bands $\ln(D_p/D_0)$ on the relative density change $\ln(P_p/P_0)$ in the orthorhombic phase of a benzene crystal. Solid line—approximation by the power law $D_p/D_0 \propto (P_p/P_0)^{3.7 \pm 0.1}$, dashed—contribution of the principal terms $D_p/D_0 \propto (P_p/P_0)^2$ of the Van der Waals interaction.

The dependence of the static displacement D_p/D_0 of the exciton bands on the relative change P_p/P_0 of the crystal density is shown for this crystalline phase in Fig. 4 also in log-log scale. It was determined using the value $D_0 = 250$ cm^{-1} corresponding to the vapor–crystal shift at normal pressure.[12] The quantity D_p was defined as the vapor–crystal displacement at a pressure p relative to the position of the vibronic M band. The displacement of the exciton bands is described by the power-law relation $D_p/D_0 \propto (P_p/P_0)^{3.7 \pm 0.1}$, represented by a solid line in Fig. 4, where the dashed line shows the relation $S_p/S_0 \propto (R_0/R_p)^6 = (P_p/P_0)^2$ that describes the contribution of the principal terms of the Van der Waals interaction.

Similar results were obtained also for the monoclinic phase of benzene. The relative changes of the volume, of the factor-group splitting, and of the static displacement of the exciton bands, were referred to the corresponding values at the phase-transition point: P_p/P_T:S_p/S_T:D_p/D_T. Figure 5 shows in log-log scale the dependence of the factor-group splitting S_p/S_T of the exciton bands on the relative density change P_p/P_T in the monoclinic phase of a benzene crystal. It is described by the power-law relation $S_p/S_T \propto (P_p/P_T)^{7.2 \pm 0.7}$, drawn solid in the figure, while the dashed line corresponds to the octupole-octupole approximation of the resonant interaction. Figure 6 shows in the same scale the dependence of the static displacement D_p/D_T of the exciton bands on the relative density change P_p/P_T in the monoclinic phase. It is described by the power-law relation $D_p/D_T \propto (P_p/P_T)^{4.5 \pm 0.1}$, shown solid in the figure,

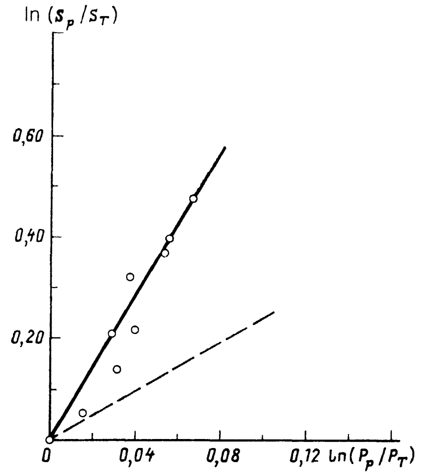

FIG. 5. Dependence of factor-group splitting $\ln(S_p/S_T)$ of soliton bands on the relative density change $\ln(P_p/P_T)$ in the monoclinic phase of the benzene crystal. Solid line—approximation by the power-law dependence $S_p/S_T \propto (P_p/P_T)^{7.2 \pm 0.7}$, dashed—octupole–octupole approximation $S_p/S_T \propto (P_p/P_T)^{2.3}$.

where the dashed line corresponds to the contribution of the principal terms of the Van der Waals interaction.

The results point thus unambiguously to the short-range character of the intermolecular-interaction forces in both crystal phases of benzene. They show that the energy of the molecular resonance interaction decreases much faster with increase of the intermolecular distances than might be expected from the octupole–octupole approximation of the resonance interaction. These results are close to the earlier ones for stronger transitions in naphthalene and anthracene crystals.[4,6]

All this points undoubtedly to inadequacy of describing intermolecular interaction in organic molecular crystal using an approximation with multipole expansion of the Coulomb interaction. This approximation, based on smallness of the exciton-transition dipole moments, disregards completely the real charge distribution in the molecules. Indeed, the dipole moments of the transitions are of the order of ~ 0.1 Å, considerably smaller than the molecule sizes, and formally the conditions for validity of the dipole approximation are approximately satisfied. However, the molecule dimensions are as a rule close to the intermolecular distances, and calculations of the Coulomb interaction should take into account the real distribution of the charges in the molecules. Contemporary calculations of the resonant-interaction energy, with account taken of the Coulomb interaction of the complete system of nuclear and electron charges of the two molecules,[7] yield more accurate results but do not contain in explicit form the dependences on the distances and it is difficult to compare them with the results of measurements made at high pressure.

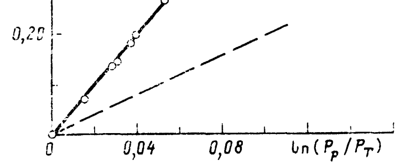

FIG. 6. Dependence of the static displacement $\ln(D_p/D_T)$ of the exciton bands on the relative density change $\ln(P_p/P_T)$ in the monoclinic phase of a benzene crystal. Solid line—approximation by the power-law dependence $D_p/D_T \propto (P_p/P_T)^{4.9 \pm 0.1}$, dashed—contribution of the principal terms of the Van der Waals approximation $D_P/D_T \propto (P_p/P_T)^2$.

It seems to us that the experimental results indicate that a substantial role is played in the formation of the exciton spectrum of the molecular crystals by the electron exchange interaction. This interaction, which is due to overlap of electron orbitals of neighboring molecules, increases rapidly with decrease of the intermolecular distances, since the electron density on the tails of the wave functions falls off exponentially. The total resonant-interaction energy consists of Coulomb and exchange components and should contain long- and short-range contributions. It is attractive from this point of view to approximate the experimental plots of Figs. 3 and 5 by the more complicated function $S_p/S_0 = A(R_0/R_p)^7 + B\exp(R_1/R_p)$, which takes both contributions into account. It should be noted, however, that such an approach is quite crude, since it presupposes an exponential exchange contribution whose exact form can be determined only by quantum-mechanical calculations. In fact, an attempt to approximate the experimental data by a function of this form does not yield positive results at reasonable values of the parameters.

We wish to note in conclusion that the experimental data obtained to date for various organic molecular crystals attest clearly enough, in our opinion, to the important role of exchange interaction, and will hopefully serve as a basis for theoretical calculations along these lines.

[1] J. M. Leger, Sol. State Commun. **66**, 245 (1988).
[2] M. M. Thiery and J. M. Leger, J. Chem. Phys. **89**, 4255 (1988).
[3] Ph. Pruzan, J. C. Chervin, M. M. Thiery, J. P. Itie *et al., ibid.* **92**, 6910 (1990).
[4] P. Sonnenschein, K. Syassen, and A. Otto, *ibid.* **74**, 4315 (1981).
[5] K. P. Meletov, Chem. Phys. Lett. **172**, 147 (1990).
[6] K. P. Meletov, Fiz. Tverd. Tela (St. Petersburg) [Sov. Phys. Solid State] in press.
[7] D. W. Shlosser and R. Philpott, J. Chem. Phys. **2**, 1969 (1982).
[8] J. A. Gizby and S. H. Walmsley, Chem. Phys. Lett. **135**, 275 (1987).
[9] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **6**, 2774 (1975).
[10] R. A. Noack and W. B. Holzapfel, in *High-Pressure Science and Technology* (Proc. 6th AIRAPT Intern. High-Pressure Conf., Boulder, CO, 1977), K. D. Timmerhaus and M. S. Barber, eds., New York, Vol. 1, p. 748 (1979).
[11] K. P. Meletov, Prib. Tekh. Eksp. No. 1, 2517 (1990).
[12] V. L. Broude, G. V. Klimusheva, A. F. Prikhot'ko *et al., Molecular-Crystal Absorption Spectra* [in Russian], Naukova Dumka, Kiev (1972), p. 47.
[13] P. W. Bridgman, J. Chem. Phys. **9**, 794 (1941).
[14] J. Akella and G. C. Kennedy, *ibid.* **55**, 793 (1971).
[15] A. S. Davydov, *Theory of Molecular Excitons* [in Russian], Nauka, 1968, p. 45.
[16] D. Fox and O. Schnepp, J. Chem. Phys. **23**, 767 (1955).

Translated by J. G. Adashko