

## Induced infrared absorption of molecular hydrogen in solid C<sub>60</sub>

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We report on the observation of induced infrared absorption in a molecular species trapped within a C<sub>60</sub> lattice. Infrared spectra for interstitial H<sub>2</sub> show distinct rotational and translational side-bands superimposed on the H<sub>2</sub>'s highly redshifted (54 cm<sup>-1</sup>) fundamental vibrational mode. Data indicate that the hydrogen is rotating almost completely freely while at the same time undergoing localized three-dimensional translational motion within the "box" formed by the C<sub>60</sub> molecules.

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It is well known that as solid C<sub>60</sub> is cooled to 260 K it undergoes an orientational phase transition from a structure in which the molecules freely rotate to one in which they undergo a ratcheting motion between orientationally equivalent positions.<sup>1</sup> Theoretical models could only explain the main features (e.g., temperature) of this transition by proposing *ad hoc* coulombic forces to supplement the graphitelike intermolecular interactions.<sup>2</sup> To date, we still lack a comprehensive understanding of the C<sub>60</sub> intermolecular potential whose importance was very recently illustrated by the discovery of superconductivity at 117 K within a doped C<sub>60</sub> lattice.<sup>3</sup>

The use of infrared (IR) spectroscopy of trapped probe molecules to study the C<sub>60</sub> intermolecular potential was first demonstrated in the pioneering work of Holleman *et al.*<sup>4</sup> They showed that the redshifted vibrational spectrum of CO trapped within the C<sub>60</sub> octahedral (*O<sub>h</sub>*) interstitial site could be explained by modeling the CO interactions with the surrounding C<sub>60</sub> molecules. They also offered the exciting suggestion that these voids would provide the ideal setting for studying quantized motion analogous to a particle in a box. The highly uniform, well-separated voids are just large enough to accept a single molecule acted upon by weak van der Waals interactions. However, despite IR studies on more than half a dozen different species, no one has yet shown evidence for quantized translational motion associated with the trapped molecules.<sup>4-6</sup>

By far the most interesting candidate to observe in these types of studies is molecular hydrogen. Due to its small mass, the rotational and translational sidebands are expected to be well separated from the main vibrational peak. In addition, there is presently great practical interest in the storage of molecular hydrogen within novel forms of carbon.<sup>7,8</sup> In an earlier paper,<sup>9</sup> we used neutron diffraction to show that under moderate loading pressures molecular hydrogen occupies a substantial fraction of the C<sub>60</sub> *O<sub>h</sub>* interstitial sites. Because H<sub>2</sub> has no dipole moment, observing its IR signal is challenging; any IR absorption arises solely through interactions with the C<sub>60</sub> lattice. Traditional methods using C<sub>60</sub> thin films do not lead to a sufficient optical path length to detect the induced absorption. Samples cannot be made any thicker because the fullerene material itself would then scatter too much of the light. In this paper, we show how the technique of diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) is ideally suited for observing weak impurity

modes in an intrinsically transparent but highly scattering host such as C<sub>60</sub>. Data taken while maintaining a constant loading pressure allow us to monitor the rate at which the H<sub>2</sub> diffuses into the C<sub>60</sub> lattice. These spectra exhibit rotational and translational sidebands superimposed on the highly redshifted vibrational mode of the trapped H<sub>2</sub> molecules. As we will show, the frequencies for all three types of excitations are consistent with existing theoretical predictions<sup>9</sup> and lead us to speculate that the C<sub>60</sub> grains may have a quasifluidlike surface layer.

We first determined the binding energy of H<sub>2</sub> within the *O<sub>h</sub>* site through a series of isotherm measurements. The C<sub>60</sub> powder obtained commercially from MER Corporation was initially heated under vacuum at 450 K for two days to remove any residual solvent. The powder was also evacuated *in situ* at elevated temperature to remove any preadsorbed gases. The hydrogen loading pressure was maintained for several hours to assure that equilibrium had been reached. The sample cell was then quenched rapidly with liquid nitrogen, kinetically locking the H<sub>2</sub> within the lattice.<sup>10</sup> The loading pressure was removed and the quantity of physisorbed hydrogen determined by warming the sample back to room temperature and monitoring the outgassing pressure within a known volume.

Figure 1 shows the isotherm curve obtained at 273 K. In

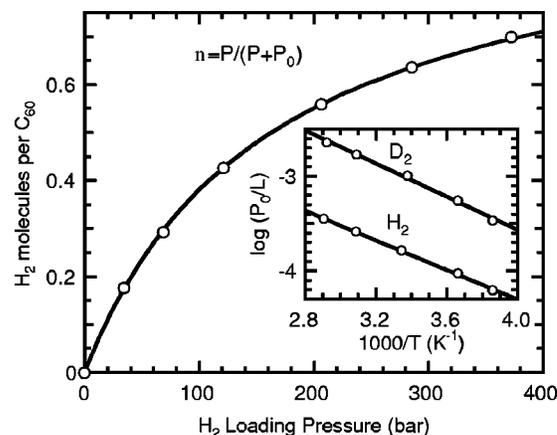


FIG. 1. Loading isotherm for H<sub>2</sub> in C<sub>60</sub> at 273 K. Data are fit to the one-parameter Langmuir model with  $P_0 = 160$  bar. The inset shows the Arrhenius plot of modified  $P_0$  for both H<sub>2</sub> and D<sub>2</sub>. Data were taken between 350 and 260 K.

contrast to previous studies<sup>11,12</sup> these results show almost perfect agreement with the standard Langmuir isotherm,  $n = P/(P+P_0)$ , where  $n$  is the fraction of the available sites filled,  $P$  is the pressure of the gas, and  $P_0$  is a characteristic pressure determined by the interactions of the gas-host system. The isotherm data asymptotically approach  $1.0 \pm 0.05$  H<sub>2</sub> per C<sub>60</sub> in agreement with the fact that the lattice contains one  $O_h$  site per C<sub>60</sub> molecule. This confirms that there is no significant trapping of the H<sub>2</sub> within the grain boundaries of the powder. For an ideal gas, it is known that within the Langmuir model<sup>13</sup>

$$P_0 = \frac{k_B T}{V_G} \frac{Z_G}{Z_A}, \quad (1)$$

where  $T$  is the temperature,  $V_G$  is the gas volume, and  $Z_G$  and  $Z_A$  are the partition functions of the gas and the adsorbed species respectively. The C<sub>60</sub> potential causes only small changes to the hydrogen's internal degrees of freedom and so to a good approximation  $Z_A^{int} = Z_G^{int}$ . Thus,

$$P_0 = \left( \frac{M}{2\pi\hbar^2} \right)^{3/2} (k_B T)^{5/2} [1 - e^{-\hbar\omega/k_B T}]^3 e^{-E_b/k_B T} \\ = L(T) e^{-E_b/k_B T}, \quad (2)$$

where  $E_b$  represents the energy difference between the gas molecule at rest and the bound molecule at its zero-point-energy, and we have assumed the trapped molecule undergoes three-dimensional isotropic simple-harmonic motion with translational frequency determined by our own IR measurements. Within the measured temperature regime the defined quantity  $L(T)$  produces only a small correction to the standard Arrhenius approach, in which the temperature dependence of the preexponential factor is ignored completely. From the slope of the inset in Fig. 1 we obtain values for  $E_b$  of 68 and 75 meV for H<sub>2</sub> and D<sub>2</sub>, respectively. The slightly greater binding energy for D<sub>2</sub> arises from its smaller zero point energy. Adding on the zero-point energy of  $3/2\hbar\omega$  (24 and 17 meV for H<sub>2</sub> and D<sub>2</sub>, respectively) yields an adsorption well depth of 92 meV. This compares well with the theoretically predicted value of 102 meV.<sup>9</sup>

The IR spectra were taken using a Bomem DA3 spectrometer with a liquid-nitrogen-cooled MCT detector and KBr beamsplitter. The DRIFTS accessory included a ZnSe dome that allowed spectra to be taken with gas pressures as high as 100 bar. Figure 2 shows a series of room temperature spectra taken while subjecting the C<sub>60</sub> powder to H<sub>2</sub> at a loading pressure of 70 bars. The spectra, referenced to that of the pure C<sub>60</sub>, contain a series of bands in the region of the H<sub>2</sub> fundamental vibrational mode at 4161 cm<sup>-1</sup>. The bands grow in intensity as the hydrogen gas slowly diffuses into the C<sub>60</sub> lattice. The time constant for this process agrees closely with unloading results obtained using proton NMR.<sup>14</sup>

The bands in the successive spectra appear to scale in intensity without any broadening, shifting, or splitting of the peaks with increasing hydrogen concentration. The smaller features marked with arrows appear to reach saturation with a somewhat faster time constant; however, the overlapping

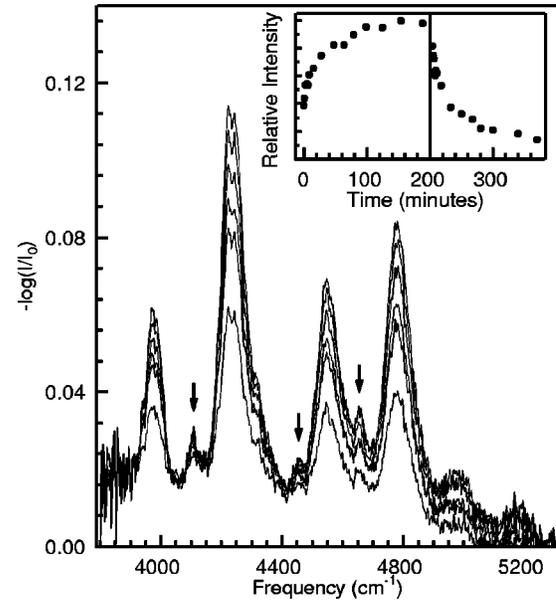


FIG. 2. Room temperature DRIFTS spectra of H<sub>2</sub> in C<sub>60</sub>. The spectra taken at 4 cm<sup>-1</sup> resolution are referenced to that of pure C<sub>60</sub> and are taken with a H<sub>2</sub> loading pressure of 70 bars. After 200 min the loading pressure is released. The inset shows the integrated sum of all the H<sub>2</sub> bands between 3800 and 5300 cm<sup>-1</sup>.

nature of the peaks makes it difficult to deconvolute the individual intensities. The inset shows the sum of the integrated intensity for all of the bands as a function of time. After 200 min the system had reached equilibrium, at which point the loading pressure was removed and the H<sub>2</sub> allowed to diffuse out of the sample. In contrast with results reported for neon,<sup>15</sup> we see no major difference between the kinetics for loading and unloading. The intensity of the peaks shows a rapid initial change followed by a much slower tail towards equilibrium. Similar two time-constant kinetics have been observed for oxygen diffusing into the C<sub>60</sub> lattice.<sup>16</sup>

Neglecting rotational distortion effects, the energy of a free hydrogen molecule in its electronic ground state can be written as

$$E_{\nu,J} = (\nu + 1/2)\nu_0 + B_\nu J(J+1), \quad (3)$$

where  $\nu$  and  $J$  are, respectively, the vibrational and rotational quantum numbers,  $\nu_0 = 4161$  cm<sup>-1</sup>, and the rotational constant  $B_\nu = 59$  and  $56$  cm<sup>-1</sup> for hydrogen in its ground and first vibrational excited states respectively.<sup>17</sup> Quantum statistics constrain orthohydrogen with total nuclear spin 1 to have odd values of  $J$ , and parahydrogen with total nuclear spin 0 to have even values  $J$ . Therefore the selection rules for photon-induced transitions are  $\Delta J = 0$  ( $Q$  transitions) and  $\Delta J = \pm 2$  ( $S$  and  $O$  transitions).

Figure 3 shows our assignment of the bands in the C<sub>60</sub>-induced H<sub>2</sub> spectrum. The pattern contains a series of weak central peaks with much stronger bands symmetrically spaced on either side. The central  $Q$  bands arise from pure rotational-vibrational transitions while the symmetrical splitting of the sidebands indicates that they arise from creation ( $R$  branch) or annihilation ( $P$  branch) of localized transla-

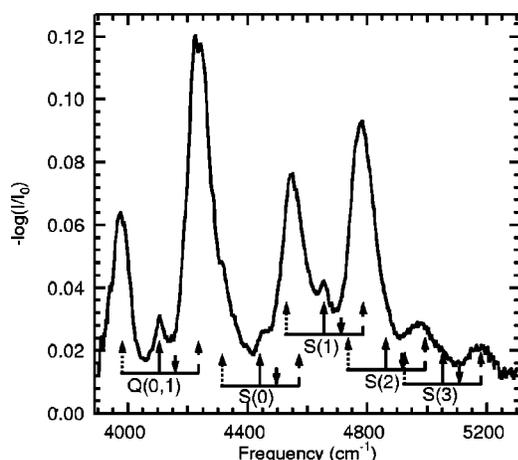


FIG. 3. Mode assignment for the  $C_{60}$ -induced  $H_2$  bands. Dotted arrows indicate  $P$  transitions, solid arrows  $Q$  transitions, and dashed arrows  $R$  transitions. The arrows pointing down show the known location of the  $H_2$  gas phase modes. In all cases the translational sidebands ( $P$  and  $R$ ) are shown at  $\pm 127$   $\text{cm}^{-1}$  relative to the pure rotational-vibrational modes ( $Q$ ), which are each redshifted by  $54$   $\text{cm}^{-1}$  relative to the gas phase. For the  $S(2)$  and  $S(3)$  transitions only the  $R$ -branch transitions are strong enough to be observed.

tional modes of the trapped  $H_2$ . In all cases, the translational sidebands are shown at  $\pm 127$   $\text{cm}^{-1}$ , in good agreement with theoretical estimates<sup>9</sup> on the order of  $110$   $\text{cm}^{-1}$ . There is also evidence (most notably in the  $Q_R$  band) of an  $18$   $\text{cm}^{-1}$  splitting in the translational sidebands which may be due to crystal-field effects.

The  $O$  transitions ( $\Delta J = -2$ ) that occur at frequencies below  $3800$   $\text{cm}^{-1}$  and are significantly reduced in intensity relative to the  $S$  transitions could not be observed due to the presence of overlapping water bands. The  $Q(0)$  and  $Q(1)$  transitions that differ by  $6$   $\text{cm}^{-1}$  in the gas phase are not resolved. As shown in Fig. 3, for each of the observed modes [ $Q(0,1)$ ,  $S(0)$ ,  $S(1)$ ,  $S(2)$ , and  $S(3)$ ], our assignment has the central pure vibrational-rotational branch shifted in frequency by the same amount,  $54$   $\text{cm}^{-1}$ , relative to the known values for gas phase  $H_2$ .<sup>17</sup> This indicates that the hydrogen is rotating almost completely freely within the interstitial  $O_h$  site with no detectable change in the rotational energy levels relative to the gas phase. This is not surprising, since the binding potential is predicted to have a small angular corrugation of only a few meV in comparison to the translational zero-point energy in excess of  $20$  meV.<sup>9</sup>

When we repeated the DRIFTS experiment with  $D_2$ , which has a reduced vibrational frequency, the presence of strong  $C_{60}$  absorption bands meant that we could only identify 3 induced  $D_2$  modes. These indicated a vibrational redshift of  $38$   $\text{cm}^{-1}$  and translational frequency of  $90$   $\text{cm}^{-1}$ , both of which are in agreement with the expected  $\sqrt{2}$  isotope effect. The  $54$   $\text{cm}^{-1}$  redshift of the  $H_2$  vibrational frequency is somewhat larger than values reported for substitutional  $H_2$  in rare gas matrices which range from  $19$   $\text{cm}^{-1}$  for Ar to  $38$   $\text{cm}^{-1}$  for Xe.<sup>18</sup> We can estimate the expected shift in our case by noting that for a highly isotropic potential, the fre-

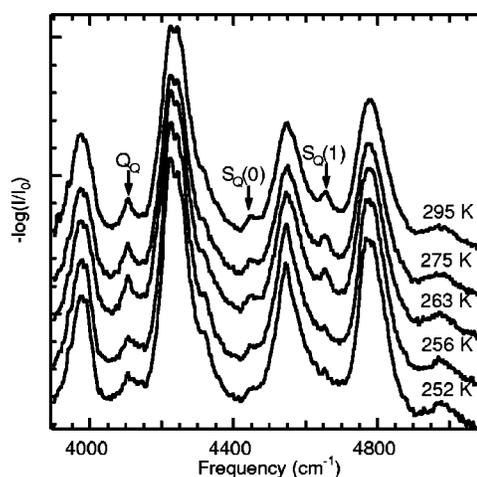


FIG. 4. Temperature dependence of the induced  $H_2$  spectrum. The  $Q$  bands indicated by the arrows show a sharp decrease in intensity on cooling through the  $C_{60}$  phase transition.

quency shift arises mainly from changes in the molecular polarizability of  $H_2$  between the ground and first excited vibrational state.<sup>19</sup> Essentially, the binding energy in the excited state is greater than that in the ground state due to its slightly increased polarizability. Using the *ab initio* determined values for the molecular polarizability of unperturbed  $H_2$  and  $D_2$  (Ref. 20) and the binding energies obtained from our isotherm measurements, we predict redshifts of  $62$  and  $44$   $\text{cm}^{-1}$  for  $H_2$  and  $D_2$ , respectively. These compare quite well with our observed values of  $54$  and  $38$   $\text{cm}^{-1}$ .

With the DRIFTS technique it is extremely difficult to obtain anything more than a qualitative explanation of the absorption intensities. However, we note that the ratio of  $R$  to  $P$  branch intensity is consistent with the detailed balance prediction of  $\approx 2:1$  at room temperature. Similarly the reduced intensity of the  $S(2)$  and  $S(3)$  bands arises because the ground states associated with these transitions are not significantly populated at room temperature.

The most surprising aspect of the spectrum shown in Fig. 3 is the presence of weak purely rotational-vibrational central  $Q$  bands (zero-phonon). An  $H_2$  molecule trapped within an  $O_h$  site experiences a centrosymmetric potential which cannot produce IR activity in these modes.<sup>21</sup> For example, in the face-centered-cubic phase of solid hydrogen only the translational sidebands are activated.<sup>22</sup> In our case the  $Q$  transitions could be activated by impurities, lattice defects, or a lack of local  $O_h$  symmetry for the interstitial site. On the rapid time scale of the  $H_2$  vibration the  $C_{60}$  molecules must be considered as stationary objects, thus modifying the local octahedral symmetry.

To distinguish between these explanations we obtained a series of spectra while cooling the system to its base temperature of  $250$  K. As shown in Fig. 4, cooling the sample to  $263$  K produced only minor changes in the overall spectrum. The only clear effect is that the lower frequency peak of the  $Q_R$  doublet becomes more intense, consistent with the changing Boltzmann population of an  $18$   $\text{cm}^{-1}$  split ground state. Cooling the sample below the  $260$  K phase transition

produced a sudden decrease in the intensity of all the central  $Q$  bands, most notably the  $S_Q(0)$  band which disappeared almost entirely.

These results rule out both impurities and lack of true  $O_h$  symmetry as the origin of the  $Q$  bands. In fact it is quite interesting to observe the decrease the intensity of a band caused by a transition to a lower symmetry state, which would be expected to enhance its mode strength. We now speculate that the  $Q$  transitions may be caused by the presence of  $C_{60}$  lattice vacancies and adatoms. Recent neutron spin echo data have shown evidence for a quasifluidlike surface layer in which  $C_{60}$  vacancies are highly mobile.<sup>23</sup> The mobility is strongest just above the phase transition and dies out for lower temperature. This behavior might also explain the two time-constant kinetics observed by several groups for the loading and unloading of gases into  $C_{60}$ . Rapid loading occurs within the surface fluid layer of a grain followed by much slower diffusion into the bulk. Morosin *et al.*<sup>15</sup> have

also reported a sudden decrease in the loading kinetics of neon on cooling through the phase transition.

In conclusion, we have shown that IR diffuse reflectance is an ideal technique for observing the quantum dynamics of gas molecules trapped within a  $C_{60}$  lattice. The same technique should work equally well with nanotubes or other novel forms of carbon. Data reveal essentially free rotational motion of the translationally bound  $H_2$  superimposed on a highly redshifted vibrational mode. The frequencies of all three types of excitations are consistent with simplified theoretical calculations and should provide accurate benchmarks for any complete theoretical model of the  $C_{60}$  intermolecular potential.

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<sup>1</sup>M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).

<sup>2</sup>S.L. Chaplot and L. Pintschovius, *Int. J. Mod. Phys. B* **13**, 217 (1999).

<sup>3</sup>J.H. Schon, C. Kloc, and B. Batlogg, *Science* **293**, 2432 (2001).

<sup>4</sup>I. Holleman, G. von Helden, E.H.T. Olthof, P.J.M. van Bentum, R. Engeln, G.H. Nachttegaal, A.P.M. Kentgens, B. H. Meier, A. van der Avoird, and G. Meijer, *Phys. Rev. Lett.* **79**, 1138 (1997).

<sup>5</sup>G.E. Gadd, M. James, S. Moricca, D. Cassidy, P.J. Evans, B. Collins, and R.S. Armstrong, *J. Phys. Chem. Solids* **59**, 1383 (1998).

<sup>6</sup>G.E. Gadd, P.J. Evans, S. Kennedy, M. James, M. Elcombe, D. Cassidy, S. Moricca, J. Holmes, N. Webb, and A. Dixon, *Fullerene Sci. Technol.* **7**, 1043 (1999).

<sup>7</sup>C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, and M.S. Dresselhaus, *Science* **286**, 1127 (1999).

<sup>8</sup>Y. Ye, C.C. Ahn, B. Fultz, J.J. Vajo, and J.J. Zinc, *Appl. Phys. Lett.* **77**, 2171 (2000).

<sup>9</sup>S.A. FitzGerald, T. Yildirim, L.J. Santodonato, D.A. Neumann, J.R.D. Copley, J.J. Rush, and F. Trouw, *Phys. Rev. B* **60**, 6439 (1999).

<sup>10</sup>A.I. Kolesnikov, V.E. Antonov, I.O. Bashkin, E.G. Ponyatovsky, A.Y. Muzychka, A.P. Moravsky, G. Grosse, and F.E. Wagner, *Physica B* **234**, 10 (1997).

<sup>11</sup>B. Morosin, J.D. Jorgensen, S. Short, G.H. Kwei, and J.E. Schirber, *Phys. Rev. B* **53**, 1675 (1996).

<sup>12</sup>Good agreement with the Langmuir model is extremely sensitive on measuring the absolute volume of the outgassing cell. In our earlier paper (Ref. 9) we inaccurately measured this volume, leading us to mistakenly conclude that the isotherm did not follow the Langmuir predictions.

<sup>13</sup>V. Bortolani, N.H. March, and M.P. Tosi, *Interaction of Atoms and Molecules with Solid Surfaces* (Plenum Press, New York, 1990).

<sup>14</sup>R. Assink, J.E. Schirber, D. Loy, B. Morosin, and G. Carlson, *J. Mater. Res.* **7**, 2136 (1992).

<sup>15</sup>B. Morosin, Z. Hu, J.D. Jorgensen, S. Short, J.E. Schirber, and G.H. Kwei, *Phys. Rev. B* **59**, 6051 (1999).

<sup>16</sup>E.A. Katz, A.I. Shames, D. Faiman, S. Shtutina, Y. Cohen, S. Goren, W. Kempinski, and L. Piekara-Sady, *Physica B* **273**, 934 (1999).

<sup>17</sup>S.L. Bragg, J.W. Brault, and W.H. Smith, *Astrophys. J.* **263**, 999 (1982).

<sup>18</sup>M.E. Alikhani, B. Silvi, and J.P. Perchard, *J. Chem. Phys.* **90**, 5221 (1989).

<sup>19</sup>D.M. Bishop, *J. Chem. Phys.* **98**, 3179 (1993).

<sup>20</sup>W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **46**, 1426 (1967).

<sup>21</sup>G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company Inc., New York, 1996).

<sup>22</sup>J.V. Kranendonk, *Solid Hydrogen: Theory of the Properties of Solid  $H_2$ ,  $HD$ , and  $D_2$*  (Plenum Press, New York, 1983).

<sup>23</sup>V.T. Lebedev, D.N. Orlova, A.I. Sibilev, G. Torok, L. Cser, V.P. Budtov, and A.V. Polyakov, *Mol. Mater.* **13**, 123 (2000).