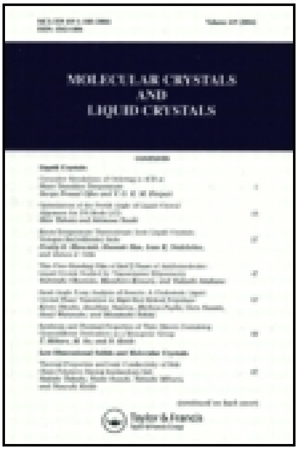

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Structure of 4,4′-Dichlorobenzophenone: Implications for Low Temperature Transport of Triplet Excitations

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Structure of 4,4′-Dichlorobenzophenone: Implications for Low Temperature Transport of Triplet Excitations

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As inferred from our x-ray single-crystal diffraction data, the microscopic mechanism of the structural phase transition at 190 K in 4,4′-dichlorobenzophenone is such that certain structural imperfections must be inevitably present in the low-temperature phase. These defects can be the physical cause behind the shallow X-traps for triplet excitons, as observed in luminescence spectra.

Keywords: 4,4′-dichlorobenzophenone; structure; phase transition; intrinsic defects; exciton traps

The carbonyl crystals are considered to be the best model solids for studying triplet excitations in organic materials [1]. Among these, 4,4'-dichlorobenzophenone (DCBP) has been thoroughly investigated by numerous techniques (fluorescence and Raman optics, NMR, x-ray, etc.) [2-5]. One of the objectives of those studies was to understand the structure of the solid and its consequences for the triplet exciton band configuration and transport. Low-temperature phosphorescence data for DCBP provide arguments that the shallow traps (the so called X traps)

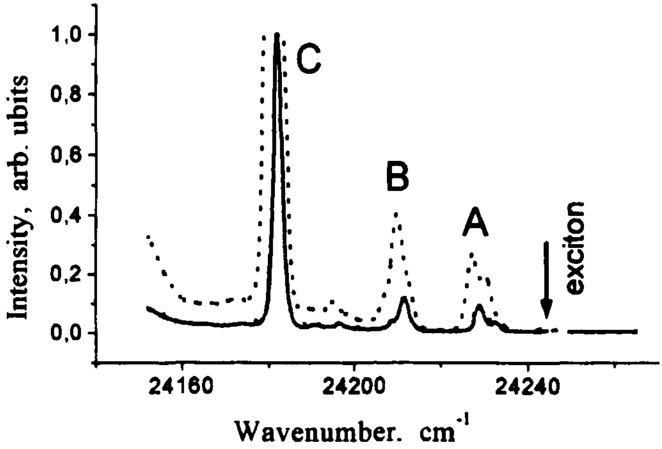

FIGURE 1 DCBP phosphorescence spectra at 1.4 K: The solid curve is for 0 → 0 transitions; the broken curve is for 1 → 0 transitions. The latter is shifted to lower frequencies by the value 1670 cm^{-1} characteristic of the carbonyl group [6].

for excitons, which are close to the exciton band bottom, are intrinsic, i.e. are due to structure faults. In particular, this can be inferred from the fact that phosphorescence spectra for X-traps have the same vibronic structure (Fig.1) and are strongly polarized along axis *c* [5].

Elucidation of the nature of the above X-traps for triplet excitons still remains a challenge. A model was suggested for the X-trap that lies 65 cm^{-1} below the exciton band bottom (trap C in Fig. 1). This trap was assumed to associate with a stable lattice defect which is an overturned molecule; calculations [5] do not contradict the phosphorescence data.

Triplet exciton transport in DCBP is usually studied at low temperatures. As the temperature is lowered to 190 K the crystal undergoes a phase transition [7,8], which can cause intrinsic X-traps to form.

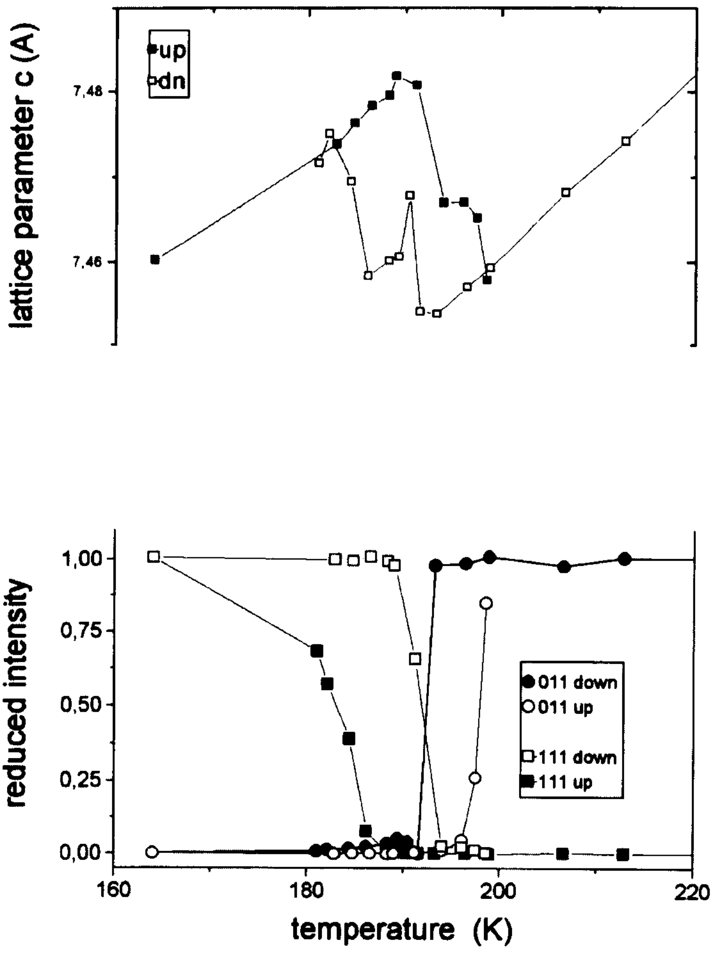

FIGURE 2 Temperature variations across the transition of: (upper) the lattice parameter *c* and (lower) the intensities of symmetry-sensitive reflections for cool-down and warm-up.

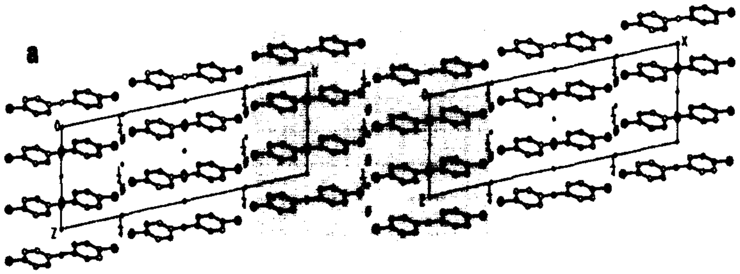

FIGURE 3 A slip, or translational twin (shaded area), in a crystal in the otherwise perfect HT phase.

The phase transition occurs from the high-temperature (HT) monoclinic phase C2/c to a low-temperature (LT) phase, which in the physically same setting is monoclinic I2/c. Detailed analysis [8,9] of the temperature behavior of intensities (Fig. 2) suggests that the transformation occurs by shifting one part of the crystal respective to the other one along axis *c* by half of the lattice period. Such a slip (Fig. 3) can be treated as an elementary phase transition act. Owing to the negative sign of the change of the lattice parameter *c* across the transition (see Fig. 2), this case differs from other similar martensitic transitions in that the elastic deformation around a slip is such [8] that it does not favor thermodynamically the formation of another slip in its closest vicinity. Thus, the slips do not bunch into lamellar domains of the new phase but, on the contrary, interact repulsively [9]. Hence, as the temperature is lowered, every next slip (provided their number is small enough) tends to form far from the already existing ones. As the transformation progresses and the number of slips becomes large, the thermodynamic force urges them to form closer to one another till the new phase fills the entire sample. However, the LT phase can form an ideal regular array only if every second layer is displaced. Since the distribution of *bc* slips at the initial stages of the phase transition is random, a certain amount of faults inevitably remains, the respective concentration on the order of magnitude being proportional to $(N)^{-1/2}$ where N is the number of *bc* layers in the sample. Theses lattice defects can be intrinsic traps for excitons.

It is commonly accepted that the triplet state is centered at the C=O bond. This state is split into a band about 8 cm^{-1} wide [10] due to resonance exchange between neighboring molecules. Since the phenyl rings are turned out of plane, the coordination of this bond with the fraction of both adjacent rings is slightly unfavorable, moreover, it cannot be brought to an optimum position to "satisfy" both rings. Over the entire temperature range from room temperature down to 164 K the R ellipsoid of the oxygen is manifestly anisotropic, showing a larger sway in the direction normal to the average molecular plane. This invokes the idea of two closely spaced minima for the orientation of the C=O bond. Thus, one can expect another phase transition to a state of ordered C=O bond orientations. Since the respective energy gain is small, the critical temperature will be low (unfortunately, we could not carry out structure measurements below 90 K). At higher temperature both minima are occupied equally but at low temperature the system has to choose between the two equal possibilities.

The DCBP molecule has two enantiomers, that is species with the phenyl rings turned out of plane in opposite directions. It is interesting that every crystallographic row of DCBP crystal comprises enantiomers stacked alternatingly. An enantiomer placed in the lattice improperly represents an unusual point defect which is stable at low temperatures.

The trapping energy for the enantiomer defect can be roughly estimated from the following considerations. In contrast to overturned molecules, the strong dipoles at C=O bonds are in this case virtually unperturbed and the main contribution to the polarization energy comes from the substantially weaker dipoles at Cl-C bonds. Hence, the binding energy is lower (10-20 cm^{-1}) than for overturned molecules [5] and the A and B traps in Fig. 1 can be ascribed to enantiomer defects.

Summing up, from x-ray diffraction data we conclude that intrinsic lattice defects can appear in the DCBP crystal undergoing the phase transition at 190 K. The defects are mismatch *bc* planes, improperly placed enantiomers, and random disruptions in the ordered array of C=O bond orientations. All the defects are expected to produce for excitons a binding by an order of magnitude lower than for "strong" defects.

References

[1] I. Y. Chan, *Rev. Chem. Intermediates*, **8**, 339 (1987).

[2] H. Nakayama, T. Eguchi, and N. Nakamura, *J. Mol. Struct.* **345**, 273 (1995).

[3] P. Peretti and P. Ranson, *J. Raman Spectrosc.* **8**, 209 (1979).

[4] A. E. Wolfenson, D. J. Pusiol, and A. A. Brunetti, *Z. Naturforsch. Teil A* **45**, 334 (1990).

[5] A. A. Avdeenko, L. M. Buravtseva, V. S. Gorobchenko, V. V. Eremenko, S. V. Izvekov, A. E. Kravchenko, O. S. Pyshkin, and V. I. Sugakov, *Low Temp. Phys.* **23**, 247 (1997).

[6] G. McGlyn, T. Adzumi, and K. Kinosita, *Molecular Spectroscopy of the Triplet State*, Pretence-Hall (1969).

[7] F. J. Zúñiga and A. Criado, *Acta Crystallogr.* **B 51**, 880 (1995).

[8] V. V. Mitkevich, V. G. Lirtsman, M. A. Strzhemechny, A. A. Avdeenko, and V. V. Eremenko, *Acta Crystallogr.* **B 55**, 799 (1999).

[9] V. V. Mitkevich, M. A. Strzhemechny, and V. G. Lirtsman, (to be published).

[10] P. Peretti, P. Ranson, and Y. Rousset, *Chem. Phys.* **56**, 135 (1981).