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Electron energy structure of DGN crystal from first-principal calculations

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Ab-initio calculations of band structure, density of electron states, and optical spectra of ferroelectric diglycine nitrate crystal (DGN) are presented for the first time. The investigation presented relates to the optimized structure of DGN. Peculiarities of the calculated band structure characterize DGN as a molecular crystal. Calculated optical spectra agree satisfactorily with corresponding experimental data in the photon energy range 3 – 13 eV.

Keywords: Band structure of crystalline semiconductors and insulators; Optical properties.

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I. Introduction

Diglycine nitrate, $(\text{NH}_2\text{CH}_2\text{COOH})_2\text{HNO}_3$, is a ferroelectric crystal undergoing phase transition of the order-disorder type at 206 K [1,2]. It possesses monoclinic spatial groups of symmetry 7 and 14, below and up this temperature, correspondingly. Phase transition in DGN regards as antiferroelectric, order-disorder type [1]. DGN crystal is similar to the well known ferroelectric triglycine sulphate crystal (TGS), because they are both regarded as the molecular type crystals with glycine and oxygen-anion complexes (NO_3^- in DGN, and SO_4^{2-} in TGS).

The crystal is transparent in the spectral range of 245 – 1900 nm. Dispersion of refractive indices in the range of transparency and temperature dependencies of refractive indices of DGN were studied in [3]. Principal birefringences of DGN for the wavelength $\lambda = 632.8$ nm are the following, $n_m - n_p = 0.079$, $n_g - n_p = 0.141$, $n_g - n_m = 0.070$ [4,5]. No references are known on the study of band electron structure and relevant experimental characteristics of DGN crystal.

In present communication, the results of *ab-initio* theoretical calculations of band electron structure of DGN crystal for the optimized crystal structures in ferroelectric phase are presented for the first time.

II. Investigation methods

The unit cell data of DGN crystal at 295 K and the

corresponding coordinates of atoms were taken from the paper [6]. The unit cell dimensions of DGN are the following: $a = 0.9225$ nm, $b = 0.5172$ nm, $c = 0.9459$ nm, $\beta = 97.19^\circ$. Two irreducible molecules are in the crystal's unit cell of DGN (Fig. 1).

Ab-initio calculations of the band structure and optical spectra of DGN crystal have been performed using the CASTEP code [7]. CASTEP is a first principles density functional theory (DFT) plane wave

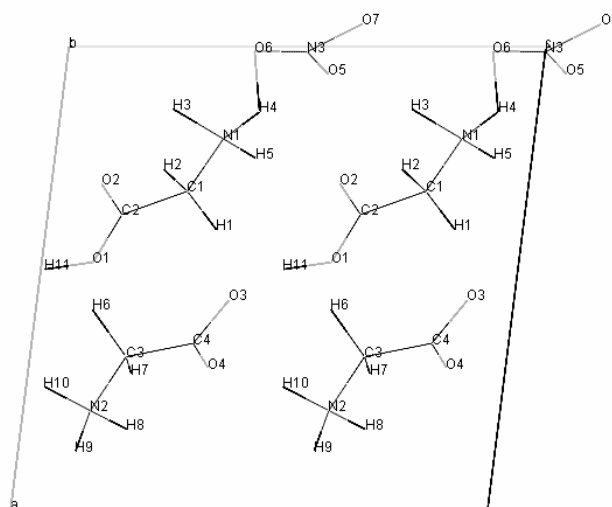


Fig. 1. View of the unit cell of DGN in the crystallographic *ac*-plane (plane of symmetry).

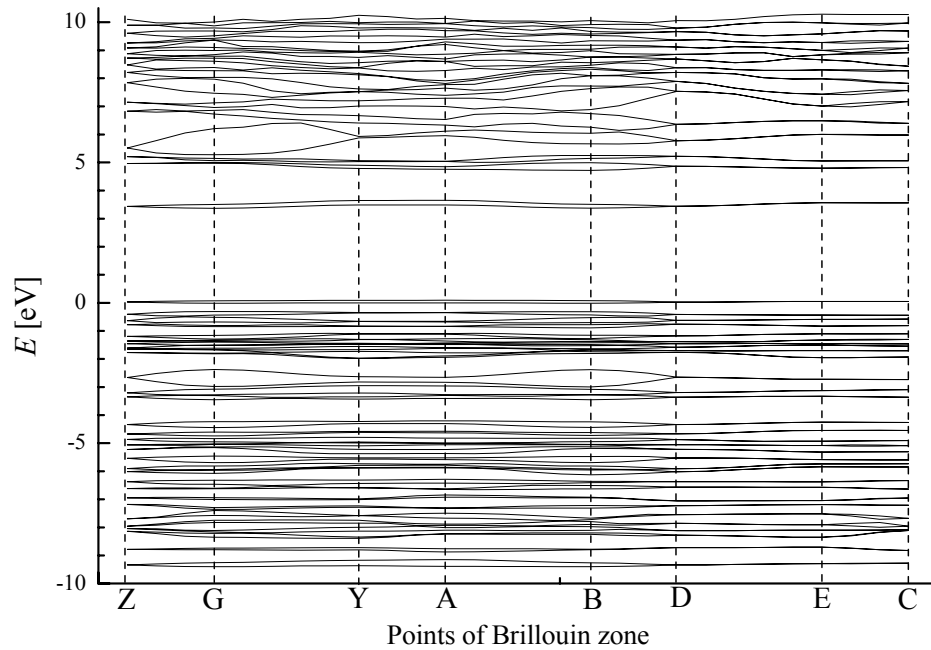


Fig. 2. Wave vector dependence of the electron energy $E(k)$ of DGN crystal: $Z - [0\ 0\ \frac{1}{2}]$, $G - [0\ 0\ 0]$, $Y - [0\ \frac{1}{2}\ 0]$, $A - [-\frac{1}{2}\ \frac{1}{2}\ 0]$, $B - [-\frac{1}{2}\ 0\ 0]$, $D - [-\frac{1}{2}\ 0\ \frac{1}{2}]$, $E - [-\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$, $C - [0\ \frac{1}{2}\ \frac{1}{2}]$. $[k_x, k_y, k_z]$ are electron wave vector components in first Brillouin zone.

pseudopotential simulation code. The calculations were performed in the frame of local density approximation (LDA, Perdew-Zunger parametrization) for the exchange and correlation effects. The norm-conserving Troullier-Martins pseudopotentials were used [8]. Calculations were performed with the accuracy 0.1 eV/atom for total energy convergence. The calculations presented concern to the optimized crystal structure of DGN in the ferroelectric phase (space group 7).

Experimental reflection spectra of DGN crystals were obtained in the photon energy range 6–22 eV at the incidence angle $\theta = 70^\circ$ using the vacuum ultraviolet spectrograph DFS-5 [9].

III. Results and discussion

The characteristic feature of band structure of DGN crystal in the range of -10–10 eV is the flat wave vector dependence of electron energy $E(k)$ (Fig. 2). The greatest dispersion $E(k)$ of valence bands not exceeds 0.5 eV (Fig. 2). The conductive bands dispersion in the range of 5–8 eV reaches 1.5 eV, so, it is greater than the valence bands dispersion. This means that the corresponding electronic states of DGN are not perturbed considerably by the crystalline field. The greatest dispersion of energy dE/dk for the conductive bands is observed along the segments $Z - G - Y$ and $B - D$ of the Brillouin zone (BZ) (Fig. 3).

The very flat band energy dispersion $E(k)$ of DGN crystal is similar to the typical borate crystals [10,11], where role similar to the nitrate group play the borate complexes. This may be principal factor also in the crystals of molecular type like DGN possessing strong oxide clusters NO_3^- and glycine complexes with high

degree of covalence chemical bonds.

Analysis of the energy dependence of density of states (DOS) reveals that the maximum in the range of 3–4 eV is attributed entirely to the atoms of NO_3 groups (Fig. 4). In the region of 4–8 eV, DOS is formed mainly by the glycine atomic groups of DGN crystal (Fig. 4). Relative contribution of NO_3 groups into the total DOS is approximately one order of magnitude smaller in this region.

The energy gap between the top of valence band (0.0 eV) and the bottom of conductive band (3.5 eV) is in relatively good agreement with the experimental position

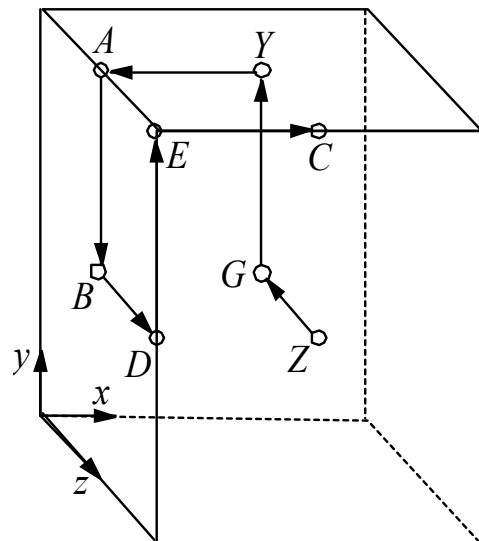


Fig. 3. Special points Z, G, Y, A, B, D, E, C in Brillouin zone of DGN crystal in ferroelectric phase

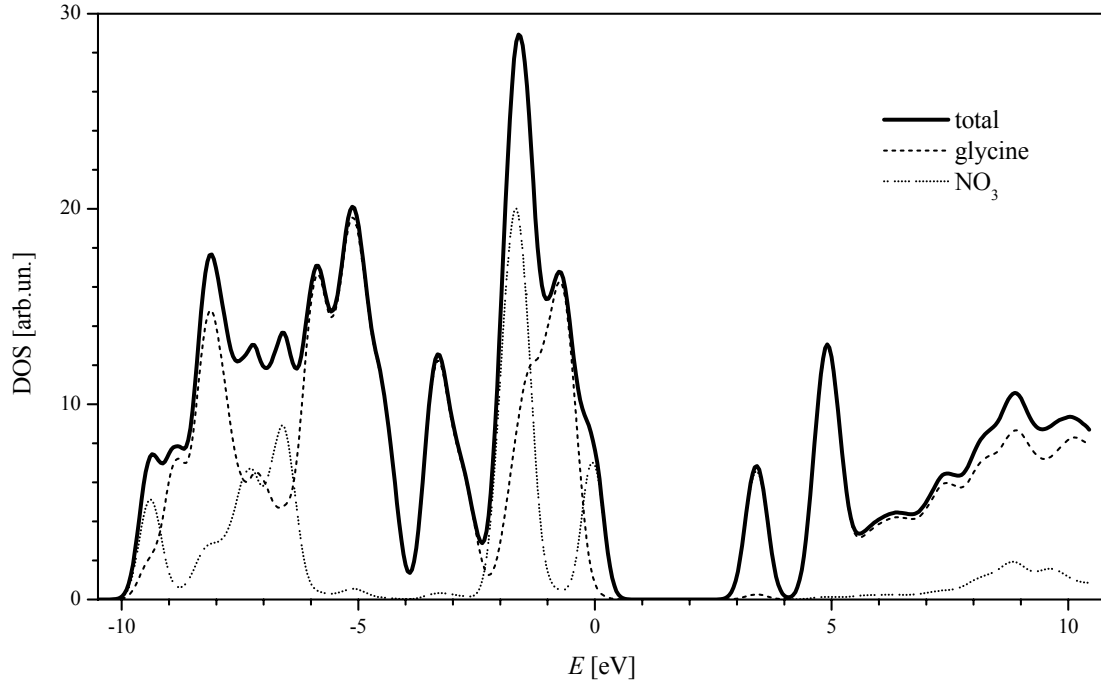


Fig. 4. Total density of electron states of DGN crystal and its projections onto glycine and NO_3 atomic groups.

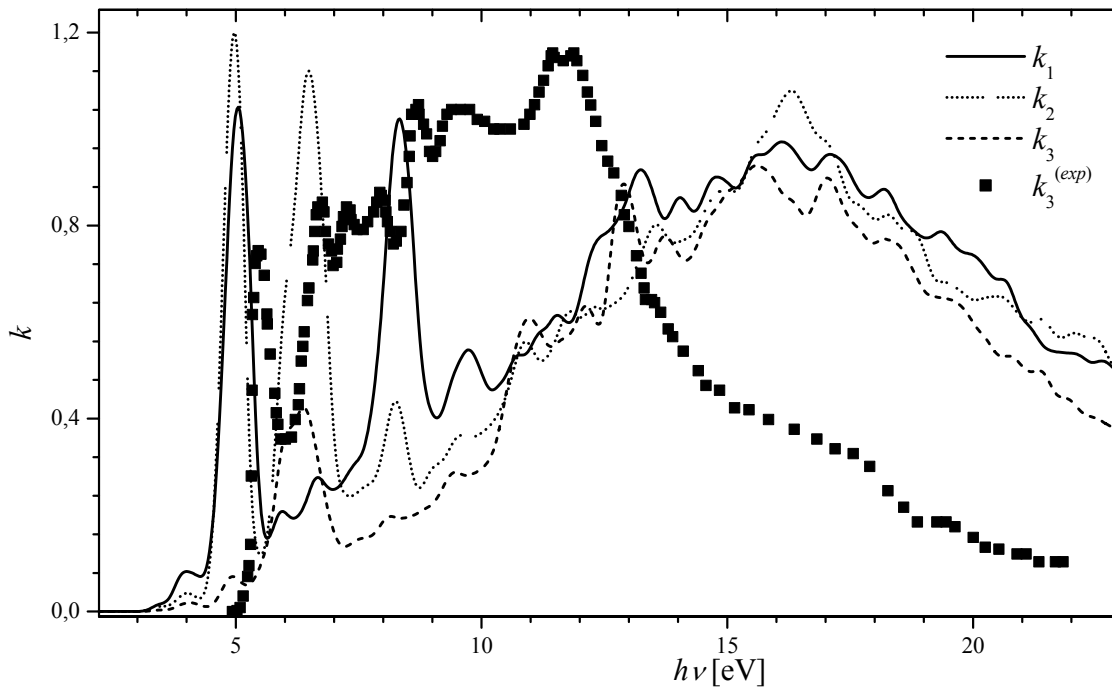


Fig. 5. Photon energy dependences of the principal absorption indices $k(E)$ of DGN crystal: k_1, k_2, k_3 – calculated using CASTEP code; $k_3^{(exp)}$ – experimental.

of weak absorption maximum at 4.2 eV and long-wavelength edge of fundamental absorption, $E \sim 5$ eV (Fig. 5).

One of the characteristic features of the band energy dispersion $E(k)$ is a degeneracy of energy states in the segment $D-E$ for both valence and conductive states (Fig. 2, 3). Almost similar degeneracy is characterized for $E-C$ segment. Both segments lie on the same boundary of the BZ (Fig. 3).

Although the band structure of DGN crystal is very flat (Fig. 2), the top of valence band is placed at A point

of the BZ, whereas the bottom of conductive zone is at G point.

Significant energy dispersion $E(k)$ is present for the valence energies near -2.8 eV. Analysis of the densities of states reveals that the states corresponding to this energy are the p -states of C1, C2, O1 and O2 atoms of the glycine complexes (Fig. 1). So, the existing crystal field in DGN is revealing in the energy dispersion $E(k)$ of the valence p -states of carbon and oxygen atoms of glycine.

It is seen from the energy dependence of DOS

(Fig. 4) that the experimentally observed weak absorption spectrum maximum at 4.2 eV is formed by the NO₃ groups of DGN crystal. The valence states in the range of -2 - -6 eV are mainly of glycine type. This peculiarity can characterize DGN as a molecular crystal, in which glycine and NO₃ groups create quasi separated states. The unoccupied states of glycine and NO₃ groups in the range of 3.0 – 6.0 eV are also quasi separated (Fig. 4).

The structures of experimental $k_3^{(exp)}(E)$ and calculated $k_i(E)$ ($i = 1, 2, 3$) optical absorption index spectra are similar in the range of 4 – 13 eV (Fig. 5). Essential differences of these spectra in the photon energy range $E > 14$ eV is probably caused by the incorrect consideration of light scattering on the sample surface during the light reflectance experiment. Analysis reveals that the calculated refractive indices are of 5 % greater than the experimental ones. This can be explained by the known fact that by DFT calculations the crystal's energy gap is often smaller than the real magnitude, and, therefore, the calculated refractive indices are greater than the experimental values.

IV. Conclusion

1. Peculiarities of the band structure and DOS confirm the molecular character of DGN crystal.

- [1] R. Pepinsky, K. Vedam, S. Hoshino, Y. Okaya. // *Phys. Rev.*, 111, pp. 430-432 (1958).
- [2] S. Hoshino, Y. Okaya, R. Pepinsky. // *Phys. Rev.*, 115, pp. 323-330 (1959).
- [3] B. Andriyevsky, Z. Czaplá, Yu. Dumka, S. Dacko, V. Kardash. // *Material Science and Engineering B* 95, pp. 14-18 (2002).
- [4] V.M. Varikash, N.A. Romanyuk, B.G. Mytsyk. // *Journal of Applied Spectroscopy*, 37, pp. 319-322 (1982).
- [5] N.A. Romanyuk, B.G. Mytsyk. // *Ukrainian Physical Journal*, 27, pp. 1206-1209 (1982).
- [6] S. Sato, J. Phys. // *Soc. Jap.*, 25, pp. 185-201 (1968).
- [7] V. Milman, B. Winkler, J.A. White, C.J. Pickard, M.C. Payne, E.V. Akhmatkaya, R.H. Nobes. // *Int. J. Quant. Chem.*, 77, pp. 895-910 (2000).
- [8] N. Troullier, José Luis Martins. // *Phys. Rev.*, B 43, p. 1993 (1991).
- [9] N.A. Romanyuk, B.V. Andrievskii. // *Optics and Spectroscopy*, 44 pp. 159-163 (1978).
- [10] I.V. Kityk, A.Mefleh. // *Physica*, B 262 pp. 170-176 (1999).
- [11] P. Smok, I.V. Kityk, J. Berdowski. // *Physica*, B 328 pp. 163-172(2003).

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Ab-initio розрахунки зонної структури, густини електронних станів, і оптичного спектру ферроелектричного подвійно-діглиційоного кристалу (DGN) представлені вперше. Дослідження презентують відносно оптимізованої структури DGN. Розрахунки зонної структури характеризують DGN як молекулярний кристал. Обчислений оптичний спектр узгоджується з експериментальними даними в діапазоні енергії фотона 3 – 13 eV.