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Molecular Cluster Approach to Magnesium and Calcium Oxide Crystals

I. Perfect Crystals

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The model of the molecular cluster (MC) is used to determine the properties of the perfect crystals MgO and CaO (the widths of the valence bands and forbidden gap, the effective charges of ions). The effective charges in the perfect crystal are shown to be ± 1.6 in MgO and ± 1.8 in CaO, which indicates high degree of covalency effects of the chemical bonding in these crystals. The obtained band widths are in reasonable agreement with the results of the other band structure calculations. The best results are obtained when the MC simulating the perfect crystal is chosen in the form of the LUC, that means that even the indirect consideration of the translational symmetry turns to be more important than that of the point symmetry.

Das Modell des Molekülclusters (MC) wird zur Bestimmung der Eigenschaften der ungestörten Kristalle von MgO und CaO benutzt (Breite der Valenzbänder und der verbotenen Zone, effektive Ionenladungen). Es wird gezeigt, daß die effektiven Ladungen in den ungestörten Kristallen $\pm 1,6$ für MgO und $\pm 1,8$ für CaO betragen, was auf einen hohen Anteil von Kovalenzeffekten der chemischen Bindung in diesen Kristallen hinweist. Die erhaltenen Bandbreiten befinden sich in vernünftiger Übereinstimmung mit den Ergebnissen anderer Bandstrukturberechnungen. Die besten Ergebnisse werden erhalten, wenn der MC, der den ungestörten Kristall simuliert, in Form der LUC gewählt wird, was bedeutet, daß sogar die indirekte Berücksichtigung der Translationssymmetrie wesentlicher ist als die Berücksichtigung der Punktsymmetrie.

1. Introduction

Magnesium and calcium oxides are divalent analogs of the alkali halides and have NaCl-type structure. These oxide crystals are usually regarded as purely ionic compounds (model $\text{Me}^{2+}\text{O}^{2-}$, $\text{Me} = \text{Mg, Ca}$). Although the free O^{2-} ion is unstable, a crystalline environment may facilitate its existence [1, 2]. The authors of the recent band-structure calculations [2, 3] have no doubt about the ionic character of the MgO crystal.

Alkali halides, being as a rule insulators, have usually rather narrow (2 to 3 eV) upper valence p-band (e.g. [4]) and a wide gap. Along with a wide gap, being typical for insulators, the MgO and CaO crystals reveal, however, a number of properties which are typical for *semiconductors* with covalent nature of chemical bonding. They are: the width of the upper valence p-band exceeding appreciably that of alkali halides, the large magnitude of the dielectric constant, etc. X-ray spectra analysis indicates also a "surprisingly high degree of covalency in MgO" [5, 6]. In [7] it is maintained that "the structure of most oxides has to be describ-

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ed on the basis of the *covalent* oxygen radius; in solids the oxygen ion is not doubly charged". At last, the authors of [6] presented contrary to the purely ionic model ($\text{Me}^{2+}\text{O}^{2-}$) a *half-ionic* one (Me^+O^-) for oxides. Their estimate shows that the existence of an anion with negative charge exceeding 1.2 is impossible²⁾ because in such a case there are no local levels in the potential well simulating the crystalline environment of this anion. However, the model employed is rather rough and uses experimental data on the charge dependence of the *free* anion ionization energy instead of that of the anion in the crystal.

Besides the model Me^+O^- is in disagreement with the well-known properties of F^+ and F centres (one or two electrons on an oxygen vacancy, respectively, i.e. the analogs of F and F' centres in alkali halides). Indeed (i) both the F^+ and F centres have *bound* ground and excited states [8] contrary to the situation in alkali halides where the excited state of F centres falls within the conduction band [9].³⁾ This is likely due to the stronger electrostatic field of the crystalline lattice in the vicinity of a vacancy in oxides allowing the latter to keep two electrons even if one of them is in an excited state. (ii) It has been shown [11] that the *g*-shift in the ESR spectra of the F^+ centre in oxides is positive contrary to the negative shift found for F centres in alkali halides. This discrepancy may be well understood theoretically basing on the F^+ centre model which involves the admixture of a charge-transfer configuration consisting of a hole shared by anions adjacent to the F centre. Such a configuration yields a positive contribution to the *g*-shift and is energetically preferable in oxides but not in alkali halides. (iii) ESR and ENDOR data [9] show that the F^+ centre wave function in oxide crystals is essentially more localized on the vacancy than the F centre wave function in alkali halides when both crystals have close lattice constants (e.g. KF and CaO). (iv) The very fact that oxides have a cubic structure argues for the *ionic* nature of the bond because for $\text{A}^{\text{IV}}\text{B}^{\text{VI}}$ crystals with essentially covalent bond a tetrahedral structure is typical.

The above-mentioned experimental facts being in disagreement with the Me^+O^- model, do not confirm however the other model $\text{Me}^{2+}\text{O}^{2-}$. It seems to be quite natural that the actual charges on ions are intermediate between ± 1 and ± 2 . It is of great interest to carry out calculations of the band structure of the perfect MgO and CaO crystals as well as of the defects in these crystals without making any a priori assumption concerning the behaviour of the charge distribution. Such an approach is necessary in order to find the precise nature of chemical bond in oxides and to check the validity of the defect calculations based on the $\text{Me}^{2+}\text{O}^{2-}$ model of the crystal.

Along with numerous calculations of defects in alkali halides and oxides, at present there exist only a few attempts to estimate the positions of their local energy levels relative to the bands of the perfect crystal. The latter is a very important property of the defect.

In order to solve these problems we employ here the molecular cluster (MC) model treating the perfect crystal as well as the point defect in the crystalline environment as large quasi-molecule (in ionic crystals the electrostatic field of the rest lattice must be added) [12, 13]. Recently, this MC model has been theoretically analysed in detail [13]. The actual calculations, being carried out

²⁾ Hereafter all charges are given in at. units.

³⁾ However, the recent photoconductivity data [10] indicate that the relaxed excited state of the F centre in MgO lies only 0.06 eV below the conduction band, i.e. is very shallow.

for perfect alkali halide [13] as well as for LiH crystals [14], confirm the ability of this model to estimate the valence band width and the energy gap, as well as to gain information about the charge distribution in the crystal. These results are in good agreement with known experimental data and band structure calculations.

The present paper uses the MC approach for perfect MgO and CaO crystals. The perfect crystal is simulated by clusters of different symmetry. It is shown that the best results are obtained with a cluster basing on the invariant Bravais parallelepiped and thus taking indirectly into account the translational symmetry of the perfect crystal.

2. MC Approach to MgO and CaO Perfect Crystals

One can conclude from experimental data (cf. [1]) that the bottom of the conduction band in MgO lies ≈ 1 eV below the vacuum level and the experimental energy gap is about 7.8 eV wide [15, 16]. In order to compare the experimental optical gap with that calculated in the one-electron approximation, one must take into account appreciable corrections due to crystal polarization by electrons and holes [17]. The recent estimate of these corrections for MgO yields $\Delta E_h = 2.8$ eV and $\Delta E_e = 1.7$ eV [18], respectively. As a result any calculated one-electron energy levels must be compared with the following band scheme (Fig. 1): the top of the upper valence band lies 11.6 eV below the vacuum level, the Hartree-Fock gap ΔE_g must be about 11.3 eV. (Unfortunately, there is no reliable experimental data concerning the width of the valence p-band in MgO and CaO.) This scheme will be used below in our analysis of MC calculation results.

2.1 Band-structure calculations of MgO

At present there exist only a few band-structure calculations of MgO and neither calculation of CaO crystal. It should be mentioned that in conventional band-structure calculations (except the tight-binding approach) the absolute values of energy levels are obtained within the accuracy of an unknown constant (for example, the zeroth Fourier component of the pseudopotential) and only energy differences can be determined unambiguously.

The band-structure calculation [1] based on the tight-binding approximation yields: the width of the 2p oxygen band $\Delta E_p \approx 9$ eV (which seems to be largely overestimated), the top of this band lies 7.6 eV below the vacuum level. (The conduction band has not been considered in [1].) The recent calculations [2] of the same author based on Green's function method yield $\Delta E_p \approx 4$ eV, the width of the 2s oxygen band $\Delta E_s = 1.4$ eV, $\Delta E_g = 5$ eV.

The empirical pseudo-potential approach [19, 20] yields $\Delta E_p = 4$ eV, $\Delta E_s = 1$ eV. The width of the energy gap has not been obtained theoretically in these

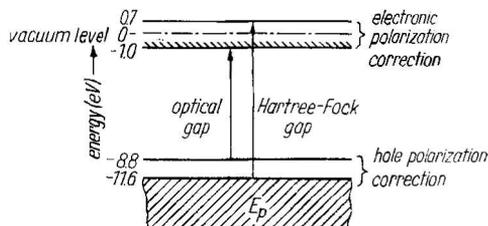


Fig. 1. The one-electron energy levels scheme of the perfect MgO crystal

calculations but its experimental estimate has been used for the form-factor determination. The simplified Hartree-Fock (HF) method using Slater exchange (without self-consistency) [3] gives $\Delta E_p = 3$ eV, $\Delta E_s = 1.5$ eV that is close to above-mentioned results [19, 20]. The magnitude $\Delta E_g = 7.5$ eV being in good agreement with the experimental energy gap is essentially less than that of the HF gap estimated above. This result is most likely caused by the use of Slater exchange. Following the above considered data (see also [21]), one can conclude that in MgO ΔE_p and ΔE_s values are 3 to 5 eV and 1 to 1.5 eV, respectively. (The appreciable discrepancy between these results and a recent calculation [22] based on the localized-orbital approach is most likely due to the method employed in [22].)

Now we turn to the calculations of perfect MgO and CaO crystals carried out in the framework of the MC model.

2.2 MC calculations for oxides

As it has been shown theoretically [13], the MC model is only applicable for crystals with sufficiently narrow (1 to 5 eV) valence bands and wide (≈ 10 eV) gaps. This is the case of alkali halides and also for the oxide crystals considered here. The molecular orbitals (MO), obtained for clusters simulating the perfect crystal, may not be strictly related to perfect crystal states unless the cluster containing a finite number of atoms has a large unit cell (LUC). Such a cluster chosen as a LUC is neutral in accordance with the binary crystal stoichiometry. However, our experience on MC calculations shows that a cluster which does not have LUC form, but is large enough, reveals groups of levels which could be put in accordance with the band scheme of the perfect crystal. (Strictly speaking, such a relation may be only done for *infinite* clusters.) Supplying the boundary conditions to the cluster with LUC, one gets naturally crystalline states corresponding to the chosen LUC [23].

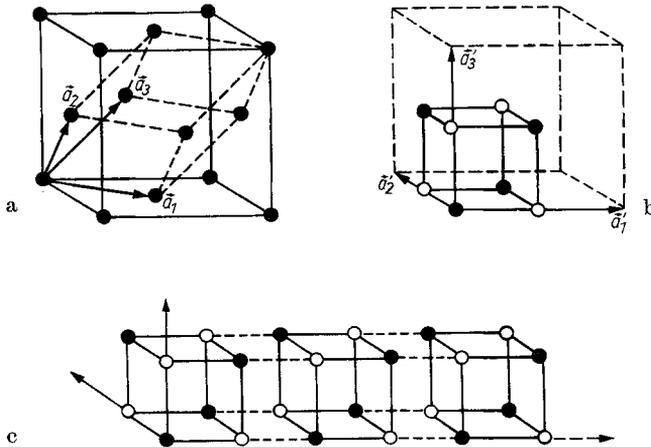


Fig. 2. a) The invariant Bravais parallelepiped (solid line) and the primitive unit cell (PUC-dashed line) on the basis of the translational vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 ; b) the invariant Bravais parallelepiped (dashed line) and the corresponding eight-atom cluster; c) cluster obtained by threefold translation of the cluster (b) along the x -axis

MgO and CaO crystals have f.c.c. Bravais lattice with the basic translational vectors $\mathbf{a}_1 = \left(\frac{a}{2}, \frac{a}{2}, 0\right)$, $\mathbf{a}_2 = \left(0, \frac{a}{2}, \frac{a}{2}\right)$, $\mathbf{a}_3 = \left(\frac{a}{2}, 0, \frac{a}{2}\right)$ (a — lattice constant) which determine the primitive unit cell (PUC) as the parallelepiped (Fig. 2a). However, the extension of PUC built up by the basis vectors leads to clusters having rather low point symmetry. This low-symmetry cluster is unable to describe the perfect crystal having high (O_h) point symmetry. Unfortunately, the NaCl structure does not allow to choose a cluster with LUC and O_h point symmetry simultaneously. Really, the 27-atom cubic cluster (three spheres surrounding the anion along with desirable O_h symmetry) has *different* number of anions and cations (13 and 14, respectively) due to which such a cluster has a total positive charge (starting from one-charged ions in alkali halides) and double charge (within $Me^{2+}O^{2-}$ model of oxides). 27-atom-cluster calculations yield good results for alkali halides [13] but, as it will be shown below, this is not the case for oxides.

So, it is desirable to combine the LUC form of the cluster and its high point symmetry. This may be done considering the invariant Bravais parallelepiped shown in Fig. 2a. This parallelepiped (being in fact a LUC) has O_h symmetry and contains four sites of the Bravais lattice. The corresponding cluster $[Me_4O_4]^0$ (Fig. 2b) consists of eight atoms and has T_d symmetry. The LUC corresponding to this eight-atom cluster has translational vectors $\mathbf{a}'_1 = (2a, 0, 0)$, $\mathbf{a}'_2 = (0, 2a, 0)$, $\mathbf{a}'_3 = (0, 0, 2a)$. (One must keep in mind the essential difference between a cluster and the corresponding LUC; they coincide only if the periodic boundary conditions are obeyed by the cluster.) The clusters $[Me_8O_8]^0$, $[Me_{12}O_{12}]^0$ (Fig. 2c) are associated with LUC's having translational vectors $(2\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3)$, $(3\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3)$, respectively.

2.3 Semiempirical method

The semiempirical method employed is based on the Mulliken-Ruedenberg approximation [24] which uses the following form of the diagonal, F_{aa} , and off-diagonal, F_{ab} , matrix elements:

$$F_{aa} = \varepsilon_{aA}(q_A) - \sum_{B \neq A} q_B \left(\chi_{aA} \left| \frac{1}{r_B} \right| \chi_{aA} \right) + V_A^M, \quad (1)$$

$$F_{ab} = S_{ab} \left\{ \varepsilon_{aA}(q_A) + \varepsilon_{bB}(q_B) + \frac{1}{2} (V_A^M + V_B^M) \right\} - T_{ab} - \sum_{C \neq A, B} q_C \left(\chi_{aA} \left| \frac{1}{r_C} \right| \chi_{bB} \right). \quad (2)$$

In (1), (2) S_{ab} , T_{ab} are the overlap and kinetic energy integrals, calculated with the atomic orbitals χ_{aA} and χ_{bB} of the atoms A and B; $\varepsilon_{aA}(q_A)$ being the valence orbital ionization potentials of the atom A having charge q_A . The values of $\varepsilon_{aA}(q_A)$ were taken from tables [25]. The one-electron three-centre integrals in (2) were expressed by the two-centre integrals following the Mulliken approximation. In the Madelung correction term $V_A^M = Mq_0/a$ the point charge q_0 was taken $\pm 1.6e$ in accordance with the charge on the central atom obtained in the 27-atom-cluster. The Löwdin population analysis [26] has been employed in the calculations of atomic charges. The 3s Me functions and 2s, 2p oxygen functions were taken from [27] in the form of linear combination of Slater type orbitals as the basic atomic orbitals.

The important fact should be emphasized that the number of electrons in the cluster with LUC form is *uniquely* determined by the number of ions in cluster independently of their effective charges. On the other hand, the number

Table 1
Energy scheme of perfect MgO and CaO crystals calculated by means of the MC method (energies in eV)

cluster	number of electrons	bottom and top of the s-band	bottom and top of the p-band	widths of s, p bands	bottom of the conduction band	energy gap	charges on atoms
$[\text{Mg}_4\text{O}_4]^0$	32	-28.4; -28.1	-12.8; -11.4	0.3; 1.4	+1.9	13.3	± 1.65
$[\text{Mg}_8\text{O}_8]^0$	64	-28.8; -28.0	-13.6; -11.3	0.8; 2.3	+1.2	12.5	$\pm 1.66; \pm 1.62$
$[\text{Mg}_{12}\text{O}_{12}]^0$	96	-28.7; -28.0	-13.7; -11.3	0.7; 2.4	+1.0	12.3	$\pm 1.65; \pm 1.61$
$[\text{Mg}_{14}\text{O}_{13}]^{2+}$	104*	-30.9; -30.0	-13.8; -6.1	0.9; 7.7	-0.4	12.3	$\begin{cases} -1.6; +1.5 \\ -1.4; +1.5 \end{cases}$
$[\text{Ca}_{12}\text{O}_{12}]^0$	96	-27.5; -26.4	-11.4; -9.7	1.1; 1.7	-0.6	9.1**)	$\pm 1.85; \pm 1.75$

*) Value corresponds to the $\text{Me}^{2+}\text{O}^{2-}$ model. This cluster exhibits also an excess level 5.7 eV above the top of the valence band (see Section 3).

**) A recent experimental estimate [16] of the optical gap is 7.085 eV, being about 1 eV less than that for MgO. Although the polarization corrections are absent for CaO, we feel that our value is underestimated.

of electrons in the charged (e.g. $[\text{Me}_{14}\text{O}_{13}]$) cluster depends directly on the ionic charges supposed.

2.4 Results for perfect oxide crystals

The clusters $[\text{Me}_4\text{O}_4]^0$, $[\text{Me}_8\text{O}_8]^0$, $[\text{Me}_{12}\text{O}_{12}]^0$ (all have LUC form) and $[\text{Me}_{14}\text{O}_{13}]^{2+}$ have been calculated by the above-described method. In Table 1 there are given results obtained for the band scheme and for charges on cluster atoms. As one can see the increase of the LUC-cluster size leads to the rapid convergence of the characteristics obtained. The width of the 2p-oxygen band in MC calculations is a little narrower than that in the above-considered traditional band-structure calculations. This is because of the fact that a cluster takes into account not all interactions of oxygen ions in the crystal. The width of the 2s-valence oxygen band $\Delta E_s = 0.7$ eV is in accordance with the mentioned band calculations.

The results for the $[\text{Mg}_{14}\text{O}_{13}]^{2+}$ cluster yield a rather reasonable width of 2s-valence band (the absolute values of energy levels are a little lowered due to the total positive cluster charge). However, the 2p-valence band is too wide and at the same time the cluster exhibits an excess level within the energy gap (see end of the Section 3). These results indicate that in oxides a cluster even containing a large number of atoms but having not LUC form yields a rather bad energy level scheme compared to the much smaller neutral cluster chosen in LUC form.

Analogous band-structure calculations for LiH have been carried out recently [14] using the same method and clusters of different type: of LUC form ($[\text{Li}_{32}\text{H}_{32}]^0$) as well as of O_h symmetry ($[\text{Li}_{13}\text{H}_{14}]^-$,

[Li₁₄H₁₃]⁺). All clusters show practically the same results contrary to those obtained here for oxides.

One can conclude that the choice of clusters in the LUC form (i.e. indirect consideration of the translational symmetry) *may be essential* in oxide (and perhaps more covalent) crystals.

2.5 Charges on atoms

The absolute values of charges on different atoms of the same cluster and for different clusters are close: 1.6 ± 0.1 for MgO and 1.8 ± 0.1 for CaO.⁴⁾ The values obtained indicate (i) the realization of an *intermediate* situation between the limiting cases Me⁺O⁻ and Me²⁺O²⁻, (ii) the appreciable covalency effects of the chemical bond in oxides (CaO is the more ionic crystal).

Also the recent theoretical estimate of oxygen charge [28] based on the consideration of [MgO₆] cluster should be mentioned. The magnitude obtained ($q = -1.4$) seems to be underestimated.

There exist also a variety of experimental estimates of ionic charges in crystals (e.g. 1.2 to 1.8 in MgO for different methods [6]) using elastic properties as well as X-ray spectra analysis. This large discrepancy reflects the fact that the ionic charge (and ion itself) in the crystal is a rather vague concept and different methods use its *different* definitions. Even within the theoretical quantum-mechanical methods the ionic charge depends, generally speaking, on the choice of population analysis [24].

When this paper has been prepared for publication paper [29] dealing with MC-CNDO/2 approach to MgO has appeared. In this connection a few comments would be desirable.

1. The HF gap (7.6 eV) obtained for a 27-atom-cluster is too narrow (cf. Section 2).

2. The authors' interpretation of the non-degenerate level lying far above the top of the valence band as an excitonic one is rather doubtful because even its existence depends on the choice of the cluster form. In our calculations this additional level appears in the 27-atom-cluster gap (and we *neglected* it as physically meaningless) but it *disappears* if the cluster has LUC form. Besides its location within the gap depends greatly on the basis choice: the exclusion of the oxygen 2s functions leads to its dramatic lowering to about 2 eV above the valence band edge. In the framework of CNDO/2 method the location of this 'floating' level within the gap depends also on the parametrization employed. The corresponding calculations carried out for the 27-atom-cluster [Mg₁₄O₁₃]²⁺ exhibit that the separation between this level and the top of the valence band is 3.07 eV or 8.65 eV if Sichel/Whitehead or Pople's parametrization is used, respectively.

3. The charges on atoms obtained (0.45 in MgO and 0.23 in LiF) being obviously unrealistic are a direct sequence of the use of traditional population analysis dealing with virtual orbitals. As it is known (e.g. [30]) such an analysis yields too high occupancies of the virtual orbitals which is due to its delocalised character. It causes rather low (and physically meaningless) atomic charges.

⁴⁾ To verify the ability of the MC model to reproduce correctly *absolute* charge values, the well-studied KCl crystal in the form [K₁₂Cl₁₂] cluster has been considered and ionic charges 0.8 ± 0.1 have been obtained in good agreement with experimental data.

3. Conclusion

MC calculations of the perfect oxides exhibit results as follows.

1. When simulating the perfect crystal by a cluster containing a finite number of atoms, it is shown, using the crystals MgO and CaO as examples, that even the indirect consideration of the translational crystal symmetry (choice of the cluster in form of LUC) turns to be more important than the total regard of the point symmetry of the crystal lattice. Clusters having not LUC form exhibit additional (and physically meaningless) levels in the band scheme. The highest possible symmetry of the cluster, having the form of LUC, would be secured when the LUC is based on the invariant Bravais parallelepiped.

2. The calculated distribution of the electronic charge in the crystals MgO and CaO (the charges on atoms are $\pm 1.6 \pm 0.1$ and $\pm 1.8 \pm 0.1$, respectively) shows that an *intermediate* situation between the model limits Mg^+O^- and $\text{Mg}^{2+}\text{O}^{2-}$ takes place. The covalency effects in the cubic crystals MgO and CaO are more appreciable than in alkali halides.

Next part of present paper deals with the F^+ and F^- centres in MgO and CaO crystals.

References

- [1] J. YAMASHITA, Phys. Rev. **111**, 733 (1958).
- [2] J. YAMASHITA and S. ASANO, J. Phys. Soc. Japan **28**, 1143 (1970).
- [3] P. WALCH and D. ELLIS, Phys. Rev. B **8**, 5920 (1973).
- [4] W. PONG and J. A. SMITH, Phys. Rev. B **9**, 2674 (1974).
- [5] G. DODD and G. GLENN, J. appl. Phys. **39**, 5377 (1968).
- [6] A. A. LEVIN, YA. K. SYRKIN, and M. E. DYATKINA, Soviet Chem. Rev. **38**, 193 (1969).
- [7] H. BLANK, Solid State Commun. **15**, 907 (1974).
- [8] A. E. HUGHES and B. HENDERSON, in: Point Defects in Solids, Vol. I, Chap. 7, Ed. J. H. CRAWFORD and L. SLIFKIN, New York 1972 (p. 357).
- [9] B. FOWLER, Physics of Colour Centers, Academic Press, New York 1968.
- [10] R. W. ROBERTS and J. H. CRAWFORD, J. Nonmetals **2**, 133 (1974).
- [11] R. BARTRAM, C. SWENBERG, and S. LA, Phys. Rev. **162**, 759 (1967).
- [12] R. P. MESSMER and G. D. WATKINS, Phys. Rev. B **7**, 2568 (1973).
- [13] A. V. BANDURA and R. A. EVARESTOV, phys. stat. sol. (b) **64**, 635 (1974).
- [14] A. N. ERMOSHKIN and R. A. EVARESTOV, phys. stat. sol. (b) **66**, 687 (1974).
- [15] R. C. WHITED and W. C. WALKER, Phys. Rev. Letters **22**, 1428 (1969).
- [16] R. C. WHITED, W. C. WALKER, and C. J. FLATER, Solid State Commun. **13**, 1903 (1973).
- [17] W. B. FOWLER, Phys. Rev. **151**, 657 (1966).
- [18] S. T. PANTELIDES, D. J. MICKISH, and A. B. KUNZ, Solid State Commun. **15**, 203 (1974).
- [19] C. FONG, W. SASLOW, and M. COHEN, Phys. Rev. **168**, 992 (1968).
- [20] M. COHEN and P. LIN, Phys. Rev. **155**, 992 (1967).
- [21] E. V. ZAROCHINTSEV and E. YA. FINE, Trans. V. Soviet Conf. Chem. Bond in Semicond., Minsk 1974 (p. 18).
- [22] S. PANTELIDES, D. MIKISH, and A. B. KUNZ, Phys. Rev. B **10**, 5203 (1974).
- [23] A. M. DOBROTVOORSKII and R. A. EVARESTOV, phys. stat. sol. (b) **66**, 83 (1974).
- [24] D. BROWN, W. CHAMBERR, and N. FITZPATRICK, Inorg. Chim. Acta Rev. **6**, 7 (1972).
- [25] C. F. MOORE, Atomic Energy Levels, in: Nat. Bur. Standards spec. Publ., Circular **1**, 467 (1949).
- [26] P. O. LÖWDIN, J. chem. Phys. **18**, 365 (1951).
- [27] E. CLEMENTI, Tables of Atomic Functions, IBM J. Res. Developm. **9**, 2 (1965).
- [28] V. H. PUCK, Soviet J. phys. Chem. **47**, 2384 (1973).
- [29] M. R. HAYNS and L. DISSADO, Theor. Chim. Acta **37**, 147 (1975).
- [30] R. A. EVARESTOV and A. N. ERMOSHKIN, Vestnik Leningr. Univ. **22**, 20 (1974).

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