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## Molecular Cluster Approach to Magnesium and Calcium Oxide Crystals

### III. Charge Distribution Analysis of Some Hole Centres

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The molecular cluster model is applied to the analysis of charge distribution and of symmetry of some hole centres ( $V^-$ ,  $V^0$ ,  $Li^0$ ,  $Na^0$ ), and also to impurity atoms of aluminium and to nitrogen ions in MgO. The calculations yield theoretical evidence of the models of hole centres derived from experimental data. Besides the essential effect of charge redistribution in the vicinity of impurity it is shown, e.g., the aluminium ion may be considered as triply charged only accounting for the charge of its nearest environment.

Модель молекулярного кластера применена для анализа распределения заряда и симметрии некоторых дырочных центров ( $V^-$ ,  $V^0$ ,  $Li^0$ ,  $Na^0$ ), а также примесных атомов алюминия и азота в кристалле MgO. Результатами расчета подтверждаются модели дырочных центров, построенные на основании экспериментальных данных. Также продемонстрировано значительное перераспределение заряда в окрестности примеси, например, ион алюминия можно рассматривать как трижды заряженный только учитывая заряд его ближайшего окружения.

#### 1. Introduction

Perfect oxide crystals MeO and those containing defects are at present the subjects of intensive experimental treatment. However, contrary to the situation in alkali halides, only a few theoretical calculations have been carried out as yet (see [1, 2] and references therein). Besides, these treatments pay main attention to the band structure of the perfect crystals and to the optical properties of the F and  $F^+$  centres [2] and do not analyse the charge distribution around the defect. On the other hand one should expect that defects, being imbedded in such rather covalent compounds with appreciable overlap of wave functions of ions, can cause a significant redistribution of the electron density in their vicinity.

The purpose of this paper is to carry out a quantum-mechanical analysis of the charge distribution in some hole centres in oxides (the energetic spectrum will not be discussed). The results obtained are compared with models postulated earlier on the basis of experimental data and confirm them.

#### 2. Preliminary Remarks

The semi-empirical quantum-chemical method employed is the same as used in [1, 2]. We restrict ourselves to MgO crystal because we are interested in models only and also because other cubic oxides exhibit similar behaviour.

The self-consistent calculation needs a fixed number of electrons in the molecular cluster ( $n$ ) which uniquely determines the total charge of the cluster. When simulating a perfect crystal by the cluster  $n$  is usually chosen following the ionic model and the fragment obtained corresponds to a closed-shell molecule with wide gap between occupied and virtual molecular orbitals (MO's).

The postulated (ionic) and obtained charges appear usually to be close. When simulating lattice defects  $n$  is uniquely determined by the total charge of the considered fragment with respect to the similar fragment of the perfect crystal. Here  $n$  should be in accordance with experimental data on the point symmetry of the centre, the existence of an ESR signal, the relative thermal stability, the optical transition energy etc. Our calculation does not involve any ad hoc suppositions concerning electronic density distribution.

### 3. Results and Discussion

#### 3.1 $V^-$ and $V^0$ centres

The intrinsic defect  $V^-$  centre has been simulated by a cubic cluster  $[\text{Mg}_{12}\text{O}_{14}]^{3-}$  containing 26 atoms around the cation vacancy (cf. [2]). The molecular orbital corresponding to the  $V^-$  ground state is doubly degenerate and contains three electrons (from four electrons allowed). Consequently this centre has a non-compensated spin and must exhibit an ESR signal which is in accordance with experimental data [3]. A comparison of the charges on atoms in this cluster and in the perfect fragment  $[\text{Mg}_{13}\text{O}_{14}]^{2-}$  shows that the hole is well localized on the six equivalent oxygen ions nearest to the cation vacancy.<sup>1)</sup> This defect has obviously  $O_h$  symmetry. However, the ESR data indicate that due to the degeneracy of the ground state the pseudo Jahn-Teller effect arises and the symmetry is lowered to the tetragonal one [4]. We have simulated this effect by outward displacement of one of the six equivalent oxygen ions. Calculations show that an 0.8 at. units displacement<sup>2)</sup> (i.e. 0.20 of the interionic distance) causes appreciable (80%) relocation of the hole charge on this anion in accordance with the model [4, 5].

The  $V^0$  centre (two holes near a cation vacancy [3]) has been simulated by a  $[\text{Mg}_{12}\text{O}_{14}]^{2-}$  cluster. Here the MO, corresponding to the ground state contains two electrons with opposite spins and this centre really has no ESR signal [3]. Charge distribution analysis shows that the second hole is well localized on the same six nearest oxygens similarly to the first one.

#### 3.2 Al Impurity and $V_{Al}$ centres

We have considered the charge distribution around the impurity aluminium ion imbedded in the MgO crystal. (It is usually thought that aluminium is introduced into the crystal in the triply charged state  $\text{Al}^{3+}$ .) The aluminium ion isolated from other defects replacing magnesium has been simulated by a cubic  $[\text{AlMg}_{12}\text{O}_{14}]^-$  cluster consisting of 27 atoms. The calculated charge on aluminium is surprisingly low, namely 0.97, i.e. lower than that of the replaced Mg ion having the charge +1.5 in a perfect crystal [1] and much lower than the expected value

<sup>1)</sup> Compare with the weak localization of the electron on an anion vacancy ( $F^+$  centre) [2].

<sup>2)</sup> This value is overestimated following data of [4] but it seems likely that it should be greater than the similar displacement of the oxygen ion in the  $\text{Li}^0$ ,  $\text{Na}^0$  centres (see Section 3.3).

+3. Such a behaviour of the aluminium ion can be understood when comparing the valence state ionization potentials (VOIP's) of aluminium and magnesium 3s atomic orbitals (AO's) corresponding to the self-consistent charges on these atoms. (The VOIP of the AO Al 3s with the charge +1 in crystal environment is equal to  $-2.87$ , being close to VOIP of 3s AO of Mg ion with the charge +1.5 also in crystal environment, which is equal to  $-3.23$  eV.)

However, further analysis indicates that six nearest anions accumulate an excess positive charge 1.2 (compared with the charge in the perfect fragment  $[\text{Mg}_{12}\text{O}_{14}]^{4-}$ ). Consequently the fragment  $\text{AlO}_6$  consisting of the impurity and its nearest environment has a total positive charge of the order of 0.8 compared with the total charge of the similar perfect fragment  $[\text{MgO}_6]$ . This result indicates that conclusions about triply charged aluminium in cubic oxides have only relative sense accounting for its nearest environment. Attempts to recalculate the charge distribution in the mentioned cluster containing aluminium adding one or two electrons lead to their localization on eight oxygens of the third coordination sphere, the charges of other ions, including the central complex  $[\text{AlO}_6]$ , are conserved. So, one cannot separately talk about a single aluminium ion carrying the charge and the hole charge in its environment but only about the charge of the indivisible formation  $[\text{AlO}_6]$  (contrary to the case of  $\text{Li}^0$ ,  $\text{Na}^0$  centres, cf. Section 3.3).

It is believed that the  $V_{\text{Al}}$  centre contains aluminium in the mentioned state instead of the previously supposed triply charged ion [6, 7]. This is not in contradiction with charge compensation and the experimental fact that the  $V^-$  centre is thermally more stable than  $V_{\text{Al}}$  [7] because a hole localized near the cation vacancy in the  $V_{\text{Al}}$  centre does not 'feel' the complex structure of the aluminium environment due to their large separation, but 'feels' only the total charge.

### 3.3 $\text{Li}^0$ , $\text{Na}^0$ centres

The impurity lithium ion has been simulated by the  $[\text{LiMg}_{12}\text{O}_{14}]^{3-}$  cluster. The effective charge of lithium appears to be 0.89, i.e. is close to the expected unit. The hole being introduced into this cluster is almost completely localized on six oxygen anions nearest to the impurity in accordance with the experimentally supposed model of this centre [8, 9]. The introduction of the hole does not change other charges. The MO corresponding to the  $\text{Li}^0$  centre ground state is doubly degenerate. Similarly to the  $V^-$  centre the pseudo Jahn-Teller effect arises, lowering the symmetry to the tetragonal one [8, 9]. The simulation of this effect by outward displacement of one oxygen up to 0.6 at. units [10] indicates the appreciable degree of localization (80%) of the hole charge on the displaced anion and a charge redistribution along the  $C_4$ -axis: the lithium charge lowers to 0.6, the charge of oxygen opposite to the displaced one becomes  $-1.7$ .

The  $\text{Na}^0$  impurity gives quite similar results, its charge in the cluster with point symmetry  $O_h$  is a little lower (0.83) than that of Li.

One defect in an anion sublattice has been considered (nitrogen impurity).

### 3.4 Nitrogen impurity

The impurity nitrogen atom has been simulated by the  $[\text{NMg}_{14}\text{O}_{12}]^+$  cluster, the obtained nitrogen effective charge is  $-2.7$ . The other charges are unchanged with respect to those of the perfect fragment, i.e. the situation is opposite to

the aluminium case. It is thought that during the growth of MgO crystals from melt the pairs of impurities (Al-N) can be formed, their spatial distribution being essentially correlated by Coulomb attraction. Our calculations indicate, however, that aluminium and nitrogen in such a pair would not be nearest neighbours.

#### 4. Conclusion

The application of the molecular cluster model to the considered hole centres in MgO crystals yields a theoretical foundation of the models built up on experimental data. The present calculations indicate that the impurity ion (e.g. aluminium) in rather covalent compounds (such as MgO) can cause appreciable charge redistribution in its environment due to which one must distinguish between an effective charge and the formal charge of the impurity ion, the latter being close to the effective charge of the fragment including the impurity and its environment.

#### Acknowledgements

One of us (E.K.) is grateful to Prof. M. I. Petrashen for grants which made possible his prolonged study at Leningrad University. The authors are grateful to Prof. Ch. B. Lushchik for helpful discussions.

#### References

- [1] A. N. ERMOSHKIN, E. A. KOTOMIN, and R. A. EVARESTOV, *phys. stat. sol. (b)* **72**, 787 (1975).
- [2] A. N. ERMOSHKIN, R. A. EVARESTOV, and E. A. KOTOMIN, *phys. stat. sol. (b)* **73**, 81 (1976).
- [3] A. E. HUGHES and B. HENDERSON, in: *Point Defects in Solids*. Ed. J. H. CRAWFORD and L. SLIFKIN, Vol. 1, Chap. 7, Plenum Press, New York 1972.
- [4] L. E. HALLIBURTON, D. L. COWAN, W. B. J. BLAKE, and J. E. WERTZ, *Phys. Rev. B* **8**, 1610 (1973).
- [5] O. F. SCHIRMER, P. KOIDL, and H. G. REIK, *phys. stat. sol. (b)* **62**, 385 (1974).
- [6] W. P. UNRUH, Y. CHEN, and M. M. ABRAHAM, *Phys. Rev. Letters* **30**, 446 (1973).
- [7] M. M. ABRAHAM, Y. CHEN, and W. P. UNRUH, *Phys. Rev. B* **9**, 1842 (1974).
- [8] O. F. SCHIRMER, *J. Phys. Chem. Solids* **32**, 499 (1971).
- [9] H. T. TOHVER, B. HENDERSON, Y. CHEN, and M. M. ABRAHAM, *Phys. Rev. B* **5**, 3276 (1972).
- [10] M. M. ABRAHAM, W. P. UNRUH, and Y. CHEN, *Phys. Rev. B* **10**, 3540 (1974).

*(Received October 11, 1975)*