Thus, although the two coefficients in (59) differ by a factor of 100, we have established the asymptotic dependence of $\langle a_{\mathbf{k}}{}^*+a_{\mathbf{k}}\rangle$ on $\mathbf{k}$ (aside, of course, from an oscillating factor which undoubtedly is not present), and shown it to be quite different from (49). It is interesting to note that (59) agrees with the asymptotic dependence of $\langle a_{\mathbf{k}}{}^*+a_{\mathbf{k}}\rangle$ in $H_1$ of Sec. 2 and hence tends to increase our confidence in the result for $m^*$ found in Sec. 3.

The same procedure can be used to calculate $\langle a_{\mathbf{k}}{}^*a_{\mathbf{k}}\rangle$ although the algebra is a trifle more involved. It is found that the asymptotic dependence of $\langle a_{\mathbf{k}}{}^*a_{\mathbf{k}}\rangle$ is the square of (59) aside from a numerical factor of order unity, a result which is anticipated by the adiabatic hypothesis.

Thus, by numerical methods one can obtain upper and lower bounds for $\langle a_{\mathbf{k}}{}^*a_{\mathbf{k}}\rangle$ for all $\alpha$ and all $\mathbf{k}$, the two bounds being farthest apart for large $\alpha$ and large $\mathbf{k}$. In field theory a quantity such as $\langle a_{\mathbf{k}}{}^*a_{\mathbf{k}}\rangle$ is, aside from an additional time dependence which can be deduced from relativistic considerations, a propagator of immediate physical interest. Unfortunately, in field theory one must face the two problems of renormalization and the fact that a ground state does not strictly speaking exist, both of which would make a lower bound a somewhat unrigorous mathematical concept. Still, the nonlinear elements in the usual field-theory Hamiltonian are positive definite so that the method of Sec. 2 may have some validity.

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# Oxygen Band in Magnesium Oxide*

Jiro Yamashita†
*Department of Physics, University of Illinois, Urbana, Illinois*

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The approximation of tight binding is employed to determine the width and the depth of the oxygen band in MgO. A width of about 9 ev and a depth of about 7.6 ev are obtained. The agreement between theory and experiment seems to be fairly good.

## INTRODUCTION

EXISTENCE of the oxygen double negative ion in oxide crystals is usually postulated and widely accepted as a useful assumption, although the free $O^{--}$ ion is not known experimentally.[1] Strictly speaking, it is more or less meaningless to speak about the existence of a particular ion within a crystal, since it is impossible to assign the electronic charge cloud to nuclei in an unique way.[2] However, we always want to have some intuitive pictures of nature, and we believe that such pictures are sometimes quite useful in the construction of suitable models for certain problems. From the point of view of the Heitler-London model, the unperturbed system consists of an assembly of independent ions in the crystal. In that sense we may imagine that the oxygen double negative ion is an independent entity in oxide crystals. In the usual cases, for example, in alkali halide crystals, the wave function of each ion in the free state is assumed to be the unperturbed wave function in the crystal. However, the situation is different in oxide crystals, where we must determine the unperturbed wave function of the $O^{--}$ ion at the outset. Although the wave function cannot be determined without more or less arbitrary assumptions, we have tried to determine the outermost wave function of the $O^{--}$ ion within the MgO crystal by a variational investigation using $2p$ orbitals.[3] Our values of the electron affinity of the ion and the diamagnetic susceptibility of the MgO crystal seem to be in good agreement with experiment. Thus, the existence of the double negative ion in oxide crystals may be a reasonable assumption in the Heitler-London model. From this point of view the MgO crystal consists of two kinds of ions, $Mg^{++}$ and $O^{--}$, which have a closed shell structure, and consequently there are no conduction electrons.

However, the band theory can also interpret the insulating properties of the MgO crystal. We suppose that the uppermost valence bands of the MgO crystal have $6N$ states, and that they are completely filled

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† On leave from the Institute of Science and Technology, University of Tokyo, Tokyo, Japan.

[1] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 82.

[2] P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd, London, 1956), Vol. 5, p. 1.

[3] J. Yamashita and M. Kojima, J. Phys. Soc. Japan **7**, 261 (1952).

with $6N$ electrons, since the crystal is an insulator. Then, we may assume that the wave functions of these bands are approximately given by LCAO Bloch functions formed from suitable atomic orbitals which have the character of $2p$ orbitals of the $O^{--}$ ion. In a first rough approximation the $2p$ orbital which has been determined by us may be useful as an atomic orbital.

The electronic structure of the valence band in alkali halide crystal and oxide crystals has been investigated by using the optical spectrum and the soft x-ray emission spectrum.[4] The observed characteristics of the electronic structure of both groups are considerably different. Alkali halide crystals have a narrow band of the order of magnitude of 1–2 ev, while oxide crystals have a wide band of the order of 7–10 ev. Although we cannot obtain the accurate value of the band width because of the widely spreading tails of the x-ray emission spectrum, the band width of the MgO crystal is estimated to be of the order of 10 ev.

Recently some experimental investigations of the electronic structure of MgO have been performed by observing photoelectric[5] and thermionic emission.[6] The results are not yet conclusive, but the bottom of the conduction band is situated at somewhat less than 1.0 ev below the vacuum level, the exciton absorption peaks at 7.5 ev and the width of the forbidden band is estimated approximately as 8.8 ev. Therefore, we suppose that the top of the valence band is at approximately 9 ev below the vacuum level. Further theoretical work on the valence band structure of the alkali halides has also been done in recent years. Casella[7] has investigated the structure of the halogen band in NaCl, and Howland[8] in KCl. However, since there has been no theoretical work on MgO, we think that it is worth while to compute the valence band structure of MgO and compare the results with experiment.

## METHOD

The approximation of tight binding is employed, and the computation is carried through for the experimental lattice distance. The crystal wave function is written as a linear combination of Bloch sums of $3N$ $2p$ orbitals of $Mg^{++}$ ion and $3N$ $2p$ orbitals of $O^{--}$ ions. The former is given by the Hartree-Fock function[9] and the radial part of the latter is given by

$$P(r)=Ar^2(e^{-2.9r}+0.15e^{-1.1r}). \qquad (1)$$

We construct the potential of the $O^{--}$ ion by using the $1s$ and $2s$ Hartree-Fock wave functions of the $O^-$ ion[10] and the $2p$ orbitals (1). As for the potential of the $Mg^{++}$ ion we adopt the Hartree-Fock potential. Then the crystal potential is constructed by summing up the potential of each ion. We calculate overlap integrals and matrix elements of the crystal potential between $2p$ orbitals of nearest neighbor ions of the opposite sign, and second nearest neighbor ions of the same negative sign. The latter is much larger than the former. Thus, we suppose that matrix elements between third neighbor ions are not important, and matrix elements between fourth neighbor ions become fairly small, and we may neglect them. Since the orbitals are $p$ type, there are two kinds of matrix element for each pair of ions; one is that for maximum overlap of the orbitals, the other is that for the minimum overlap.

For convenience, we introduce here the following notation: $E$ is the one-electron energy of the band, which is measured from the vacuum level, $E_0$ is the energy of the $2p$ orbital in the free ion, $e^2M_a/a$ is the Madelung energy, where $M_a$ is the Madelung constant and $a$ is the distance between the nearest neighbor ions. $X$ is defined by $E=E_0\pm e^2M_a/a+X$, and $\mathbf{k}$ is the wave number vector of electrons in an energy band. $S_1$ is the overlap integral between the $2p$ orbitals of second nearest neighbor $O^{--}$ ions in the maximum overlap direction, $S_2$ is the similar overlap integral in the minimum overlap direction, $T_1$ is the overlap integral between the $2p$ orbitals of the nearest neighbor ions in the maximum overlap direction, and $T_2$ is the similar integral in the minimum overlap direction. We calculate these integrals by the standard method which was developed by Löwdin and others. Further, we introduce the following quantities: $P_1$ is the matrix element of the crystal potential between the orbitals which appear in $S_1$, $P_2$ is the similar matrix element between the orbitals which appear in $S_2$, and $Q_1$ and $Q_2$ are the matrix elements of the crystal potential between the orbitals which appear in $T_1$ and $T_2$, respectively. We denote the crystal potential by $V(\mathbf{r})$ and the potential of the ion $n$ by $V_n(r)$. If we assume that the crystal potential comes from only plus and minus point charges put on the lattice sites, then we have $P_1=-S_1M_a/a$, $P_2=-S_2M_a/a$, $Q_1=T_1M_a/a$, and $Q_2=T_2M_a/a$, and consequently the energy band has no width. Thus, it is convenient to write $P_1=-S_1M_a/a+p_1$, $Q_1=T_1M_a/a+q_1$ and so on.

Calculation of $Q_1$ and $Q_2$ is not difficult, because the $2p$ orbital of the Mg ion is well localized around the nucleus. We expand the $2p$ orbital of the $O^{--}$ ion and the crystal potential around the Mg nucleus by a series of spherical harmonics and calculate the matrix element. Convergence of the series expansion is very good. On the contrary, calculation of $P_1$ or $P_2$ is not so easy, because the $2p$ orbital of the $O^{--}$ ion spreads considerably. Let us denote the $2p$ orbitals of the $O^{--}$ ion by $\varphi_z(r)$ and $\varphi_x(r)$. Then we want to calculate the

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following integrals

$$I=\int_0^\infty\int_0^\pi\int_0^{2\pi}\varphi_{z(x)}(r+R_1)\times[V(\mathbf{r})-V_0(\mathbf{r})]\varphi_{z(x)}(r+R_0)d\tau, \qquad (2)$$

where $|\mathbf{R}_0-\mathbf{R}_1|=a\sqrt{2}$.

Now, we introduce an approximation. Let us imagine a sphere of radius $r_i$ around the point $R_0$, whose surface is divided into small portions by planes of $\theta=$ constant and $\varphi=$ constant. Further, we denote the area of a small portion by $\delta_j(r_i)$ and its middle point by $A_{ij}$. Then we replace the triple integral $I$ by a double summation,

$$I\approx\sum_i\sum_j\varphi_0(A_{ij})V(A_{ij})\varphi_1(A_{ij})\delta_j(r_i), \qquad (3)$$

where $\varphi_0(A_{ij})$ and $\varphi_1(A_{ij})$ are values of $\varphi(r+R_0)$ and $\varphi(r+R_1)$ at the point $A_{ij}$, respectively, and $V(A_{ij})$ is the lattice sum of the potential of each ion at the point $A_{ij}$,

$$V(A_{ij})=\sum_{n\neq0}V_n(A_{ij}). \qquad (4)$$

In the summation, we use the actual ionic potential up to third neighbors of the $R_0$ ion and replace the potential of further ions by point charges. In order to determine the energy of the electron as a function of $k$, we must solve the six-dimensional secular equation. However, in the actual case, $q_1$ and $q_2$ are so small as compared with $p_1$ and $p_2$, that we can neglect them in the first approximation. Then, the six-dimensional determinant can be reduced, and we can easily manage it. We compute $E(k)$ curves for three directions in $k$ space, $(k,0,0)$, $(k,k,0)$ and $(k,k,k)$. As a second approximation, we modify the results by considering $q_1$ and $q_2$ as a small perturbation.

## RESULTS

After some numerical calculations, we obtain the following results: $S_1=-0.124$, $S_2=0.039$, $T_1=-0.0464$, $T_2=0.0137$, $p_1=0.047$, $p_2=-0.013$, $q_1=0.003$, and $q_2=-0.001$ in atomic units. By using these values we obtain the energy values of the electron in the valence band of the MgO crystal. We find that two sets of the bands are well separated in energy, so that we can approximately assign the upper three bands as the oxygen $2p$ bands and the lower three bands as the magnesium $2p$ bands. The upper energy bands are shown in Fig. 1 in atomic units. As seen from Fig. 1 the $2p$ $O^{--}$ valence band is very wide in energy, about 9 ev wide. The top of the valence band is situated at 7.6 ev below the vacuum level.[11] These theoretical values are in good agreement with the experiments mentioned previously. The maximum energy of the valence band appears at the point $k=0.6(\pi/a)$ in the $(k,k0)$ direction. However, it is not certain that the accuracy of the present calculation is sufficient to give reliable knowledge of the detailed structure of the band, because the structure depends sensitively upon the relative ratio of $p_1$ and $p_2$

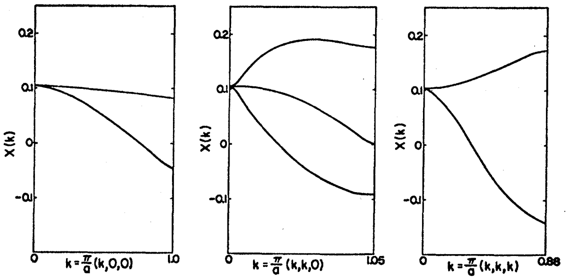

FIG. 1. Energy of the $O^{--}$ $2p$ bands in MgO for three directions in $k$ space. $X(k)$ is defined by $E(k)=E_0-e^2M_a/a+X(k)$, where $E_0$ is the energy of the $2p$ orbital in the free ion, $e^2M_a/a$ is the Madelung energy. We use here the atomic units ($e=1$, $m=1$, and $h/2\pi=1$).

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## APPENDIX

For purposes of comparison, we have done a similar computation for NaCl. We use the Hartree-Fock wave function of $Cl^-$ $3p$ and $Na^+$ $2p$ and the Hartree-Fock field also. Since calculation of the summation (3) is rather laborious, we compute the integral $I$ approximately by expanding the crystal potential around the $Cl^-$ nucleus $R_0$ by spherical harmonics. This method is less accurate than that mentioned previously. In the following we show the result. The meaning of the notation is the same as before. $S_1=-0.0741$, $S_2=0.0193$, $T_1=-0.0344$, $T_2=0.0084$, $p_1=0.0093$, $p_2=-0.0023$, $q_1=-0.00052$, and $q_2=0.00016$. The width of the valence band is estimated as about 1.7 ev. Casella has determined a minimum for the width of the halogen band in NaCl. A minimum width of about 1.0 ev was obtained by him.

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[11] As $E_0$ of the $O^{--}$ ion we use the experimental value, 9 ev. See reference 1.