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SEMI-CONDUCTORS WITH PARTIALLY AND WITH COMPLETELY FILLED $3d$ -LATTICE BANDS

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ABSTRACT. Attention is drawn to a class of semi-conductors or insulators with incompletely filled $3d$ bands. Their lack of conductivity, if the number of electrons per atom is an integer, is explained by the circumstance that a moving electron will have a large probability of being withdrawn to the initial atom, if only the potential barriers to be penetrated are sufficiently high to reduce the frequency of transition below a certain limit. This inhibiting factor disappears, if for ions of equal electronic levels the number of electrons per atom differs from an integer. In the case of NiO this condition is fulfilled if an electron is brought by thermal excitation from the lattice $3d$ band into the somewhat raised and less occupied levels a, a' (figure 1); these levels belong to Ni ions adjacent to a vacant Ni lattice point introduced by the deviations from stoichiometry, and two of these Ni ions are at the absolute zero Ni³⁺ ions. An analogous conduction mechanism holds for non-stoichiometric Cu₂O, with a completely filled $3d$ band (figure 2).

Photoconductivity is generally observed with substances with completely filled zones and never with substances of the NiO type. A tentative explanation is given for this fact on the basis of the model of figure 1 and figure 2.

In non-stoichiometric ZnO vacant oxygen lattice points are assumed (figure 3); in that case the calculation of the lattice levels shows that at the lattice holes one Zn²⁺ is converted into Zn, whereas in the lattice the additional electrons form Zn⁺ ions, as will be the case after thermal transitions of the electrons belonging to these Zn atoms into the lattice $4s$ band.

§1. CLASSIFICATION OF SEMI-CONDUCTORS

ACCORDING to the quantum theory of electronic states in solids, as developed by Sommerfeld, Bloch, Brillouin, Bethe and others^(1, 2, 3), with the special aim of understanding the electrical properties of the metals, those substances will be electrical insulators for which the number of electrons is just sufficient to fill up a number of Brillouin zones completely, and the lowest unoccupied Brillouin zone is separated from the occupied zone with the highest energy by a sufficiently broad energy gap (forbidden region). For instance the following ionic compounds NaCl, MgO, AgCl, ZnO, TlCl all contain only ions with closed electronic groups or sub groups and thus only completely filled Brillouin zones, and they are known to be very poor conductors if they are pure and of stoichiometric composition. Though, according to quantum mechanics, all the electrons of a perfect lattice are more or less free to move through the lattice, the electronic states of a completely filled energy zone cannot give rise to electronic conduction, and unidirectional transport of electrons is only possible if a zone is incompletely filled, either because the number

of electrons is incapable of filling up the zones completely, or because several zones overlap in the lattice, the electrons of one atomic level being thus distributed over more than one band or zone of lattice levels. On the basis of these conceptions Wilson⁽⁴⁾ and Fowler⁽⁵⁾ have developed a theory of semi-conductors. Wilson considers the case of two energy zones, one exactly full of electrons at absolute zero and a higher one entirely empty, separated by a narrow forbidden region. Accordingly at a higher temperature there will be a few electrons of the lower zone in the higher one, and necessarily a number of empty states in the lower zone. Both will give rise to electronic conduction, but predominantly the electrons in the higher zone, where the potential barriers are lower with respect to the electronic levels. Such semi-conductors, which owe their conductivity to thermal excitation of electrons from one energy zone into another higher one, were called *intrinsic* semi-conductors.

A substance belonging to the class of semi-conductors in which electronic conduction occurs predominantly according to the model of Wilson is probably Cu_2O of stoichiometric composition. In this compound the cuprous ion Cu^+ contains a closed $3d$ shell and an empty $4s$ shell.

Sometimes insulators of the type considered above can be converted into semi-conductors in two ways, either by small deviations from stoichiometric composition or by foreign impurities. Of these *extrinsic* semi-conductors only the first mentioned will be considered in the present discussion.

(a) There exists, however, a large class of semi-conductors of a quite different type, for which it has only been recognized incidentally that they must be treated in a way deviating fundamentally from the Wilson theory. Several substances contain atoms or ions with an odd number of electrons; then, in many cases, at any rate for substances with a simple lattice type (such as simple translation lattices, or lattices with a face centred or body centred unit cell), the amount of electrons is incapable of filling up a number of Brillouin zones completely and we have to deal with a partially occupied Brillouin zone. Nevertheless several substances, especially ionic compounds, of this type do not show a metallic conductivity, but belong to the class of semi-conductors or even insulators.

In the present paper we will restrict ourselves to compounds containing ions of the first long series of the periodic system. As examples may be mentioned MnO ($\log \rho = 8$), CoO ($\log \rho = 8$), Mn_3O_4 ($\log \rho = 7$), Fe_2O_3 ($\log \rho = 10$), CuO ($\log \rho = 7$), etc.* The electronic configurations of the cations involved can be read from table 1. This table, comprising elements which have the argon configuration $(1s)^2; (2s)^2(2p)^6; (3s)^2(3p)^6$ in common, shows the distribution of electrons between the $3d$ and $4s$ shells for a number of important atoms and ions from the part of the periodic system considered. These distributions can be derived in some cases from the spectroscopical data⁽⁶⁾ concerning the ground state of the free atoms or ions (shown in bold-faced type) and the remainder can then be derived by interpolation or (and) by taking into account the paramagnetism of the ions in the corresponding salts⁽⁷⁾. From table 1 it results that all ions present in stable chemical compounds

* The $\log_{10} \rho$ values ($\rho =$ specific resistance in ohm-cm.) are only given as integers because of the inevitable uncertainty in these data; for our considerations only the order of magnitude is significant.

in the transition region of the periodic system considered contain 3d electrons and no 4s electrons. As a consequence of this circumstance we infer that there is no great difference between substances like those mentioned above, containing odd

Table 1

Number of electrons in ion	Atomic number of atoms		18		19		20		21		22		23		24		25		26		27		28		
	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	3d	4s	
18	Ar		K ⁺		Ca ²⁺		Sc ³⁺		Ti ⁴⁺		V ⁵⁺														
	0 0		0 0		0 0		0 0		0 0		0 0														
19			K						Ti ³⁺		V ⁴⁺														
			0 1						1 0		1 0														
20					Ca				Ti ²⁺		V ³⁺														
					0 2				2 0		2 0														
21							Sc		Ti ⁺		V ²⁺		Cr ³⁺		Mn ⁴⁺										
							1 2		(2) (1)		3 0		3 0		3 0										
22									Ti		V ⁺		Cr ²⁺		Mn ³⁺										
									2 2		4 0		4 0		4 0										
23											V		Cr ⁺		Mn ²⁺		Fe ³⁺		Co ⁴⁺						
											3 2		5 0		5 0		5 0		5 0		5 0				
24													Cr		Mn ⁺		Fe ²⁺		Co ³⁺				Ni ⁴⁺		
													5 1		5 1		6 0		6 0		6 0		6 0		6 0
25															Mn		Fe ⁺		Co ²⁺				Ni ³⁺		
															5 2		6 1		7 0		7 0		7 0		7 0
26																	Fe		Co ⁺				Ni ²⁺		
																	6 2		8 0		8 0		8 0		8 0
27																			Co				Ni ⁺		
																			7 2				9 0		9 0
28																							Ni		
																							8 2		8 2

numbers of electrons, and for instance NiO, with even numbers of electrons, since the band of 3d levels contains five 3d zones and these 3d levels, coinciding in the free ions, presumably are not split up wholly into separate zones in the lattice, and all ions with an incompletely filled 3d group will therefore give rise to partially occupied energy bands in the lattice. Actually there is no great difference in the behaviour of CoO and NiO; for the latter also $\log \rho = 8$.

(b) Not all substances of the type considered are poor conductors. It is a well-known fact that both the conductivities of Cu₂O, CuJ, ZnO (with cations having a complete 3d shell, 3d¹⁰) and of CoO, NiO etc. (incomplete 3d shell) can be raised several powers of ten by small deviations from the stoichiometric composition^(8, 9, 10, 11) and it has already been suggested by Wagner that this increased conductivity is connected with quasi-free electrons or electron holes owing to the presence of ions of higher or lower valency. A very interesting case is represented by Fe₃O₄ ($\log \rho = -2$), which has a conductivity of about ten powers of ten as high as Mn₃O₄, Co₃O₄, γ Mn₂O₃, γ Fe₂O₃.

In a previous publication we have shown that the cation arrangement in the

lattice of Fe_3O_4 shows an "averaged structure" of a special type, viz. a statistical distribution of equal amounts of Fe^{2+} and Fe^{3+} ions about crystallographically identical lattice points^(12, 13); in this respect it differs from Co_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, etc. with otherwise identical or closely related crystal structures (spinel type). From this we infer that favourable conditions for electronic conduction exist, if for a band of electronic states the number of electrons per atom (ion) differs from an integer, and this is also important in relation to the conductivity of non-stoichiometric compounds.

(c) A third point, which seems to be of some importance for a comprehension of the behaviour of the substances considered, is that only those substances (stoichiometric and non-stoichiometric) show photo-conductivity, which are derived from compounds with cations containing a complete $3d$ shell, viz. CuJ , Cu_2O , ZnO . This seems to be a general rule throughout the whole periodic system, since all substances reported to be photoconductors (halides of the alkali- and alkaline earth metals and of Ag^+ , Cu^+ , Tl^+ , Hg^{2+} , Pb^{2+} ; very many sulphides, e.g. Ag_2S , Sb_2S_3 , HgS , Bi_2S_3 , PbS , Ag_3SbS_3 ; oxides like BaO , Cu_2O , Ag_2O , CdO , Sb_2O_3) contain cations (and anions) with closed electronic groups or sub-groups. No photoconductivity has been observed, as far as we know, for substances like MnO , CoO , NiO , Co_3O_4 , Mn_3O_4 , Fe_2O_3 etc.; in this laboratory Mr H. H. Kraak has investigated certain of these compounds* by irradiation with a high pressure mercury discharge lamp and has been unable to establish any effect upon their conductivity.

From this discussion, then, a number of interesting points result, which can be summarized in the following three problems:

(1) Why are several of the oxides considered here semi-conductors or almost insulators, although they contain an incompletely occupied $3d$ band?

(2) Why do exceptionally favourable conditions for electronic conduction arise if the number of electrons per atom in this band is different from an integer?

(3) What is the reason why all these substances do not show photoconductivity, whereas those substances containing a completely filled $3d$ band are all photoconductors?

In the following sections we shall consider these substances from the point of view of their electronic bands and the relations between them.

§2. LATTICE DEFECTS

The nature of the lattice deviations involved in deviations from the stoichiometric composition and their significance for electronic conduction have been discussed in detail by Wagner⁽¹⁰⁾. Also in our case we must consider beforehand what changes occur in the lattices of the substances investigated, if the composition is made different from stoichiometry. For our present purpose, we need not consider the small deviations from the perfect lattice, which are present in every real lattice owing to the thermal equilibrium corresponding to the previous thermal history⁽¹⁴⁾.

* Namely NiO , NiO containing some oxygen in excess, Co_3O_4 and Mn_3O_4 as pressed bars.

Greenish NiO can be transformed by oxidation into black "NiO" and then contains a small amount of oxygen (e.g. 0.5 per cent) in excess. The extra oxygen may be located between the normal lattice ions (interlattice points), but owing to the small polarizability of the oxygen it is much more likely that the lattice contains vacant nickel lattice points, whereas the additional oxygen is located at normal lattice points. This view is substantiated by the work of Jette and Foote⁽¹⁵⁾, who investigated the crystal structure of Wüstite ("FeO"). A phase of pure FeO is not stable under any conditions; for the Wüstite phase, if prepared at 1050°, they found solid solutions containing 76.7–76.1 per cent Fe, i.e. from Fe_{0.94}O to Fe_{0.91}O. These phases contain vacant positions in their cation lattice; the latter phase for example contains therefore an averaged distribution of $\frac{8}{11}$ Fe²⁺, $\frac{2}{11}$ Fe³⁺ and $\frac{1}{11}$ vacant lattice points per oxygen ion about the normal cation position.* Also pure NiO seems to be unstable⁽¹⁶⁾, and identical relations may be expected here, though the deviations from stoichiometry are less than in the case of FeO.

For NiO with an oxygen excess we must therefore assume vacant points in the cation lattice. Such an assumption can also safely be made for the case of CuJ with a small excess of iodine, in view of the large radius of the J⁻ ion. For Cu₂O the same view has been advocated by Dünwald and Wagner⁽¹⁷⁾. It has generally been assumed in these substances containing a metal deficit that the excess of negative charge originating from the excess of anions is neutralized at the cations, i.e. by the formation of cations of higher valency (Fe³⁺, Ni³⁺, Cu²⁺); in the present cases this conception seems quite reasonable on the basis of chemical arguments, but the possibility that anions of a lower charge (eventually neutral atoms) are formed cannot be excluded *a priori*. Indeed, in KJ containing a small excess of iodine, no K²⁺ ions but J atoms are formed. This can easily be ascertained, however, for every case, by considering to what extent the various electronic levels are shifted in the lattices: the electrons will be removed from the *highest occupied* level. The results of such calculations are summarized in table 2. These calculations yield, of course, the positions that the levels would have, if they were not broadened by the lattice (in the following we denote these positions as "centres" of the bands). We also include the calculations of the electronic levels of ions adjacent to a vacant lattice point, for electrons must be removed as a consequence of the disappearance of a number of cations from the lattice and it is generally more favourable to remove these electrons from a cation that is adjacent to such a lattice hole. For the case of Cu₂O Schottky and Waibel⁽¹⁸⁾ assumed therefore that Cu²⁺ ions are located directly adjacent to a vacant Cu⁺ lattice position. For instance, for NiO (NaCl lattice type), where each vacant Ni point is surrounded by 12 nickel ions, we wish to consider the case that two of these nickel ions yield an electron and become Ni³⁺ ions, in order to counterbalance the absent Ni²⁺. Neglecting polarization energies we see that such a Ni³⁺ is surrounded by a normal lattice minus one Ni²⁺ at a distance $r\sqrt{2}$ (r = shortest Ni-O distance) and plus one positive charge at $2r\sqrt{2}$ (in the most favourable state), hence the *Madelung* energy for one electron at the lattice point considered (Ni³⁺ ion

* Another possibility is that the Fe³⁺ seek different interstices, but presumably it can be excluded by the fact that no complete series of solid solutions with Fe₃O₄ exists.

Table 2

NiO		
Lattice type: NaCl ₁ Shortest distance Ni to O Distance Ni ³⁺ to lattice hole Distance Ni ³⁺ to Ni ³⁺ Madelung constant Third ionization energy Ni (<i>I</i> ₃) Second electron affinity O (<i>E</i> ₂)	$a = 4.17 \text{ \AA.}$ $= 2.09 \text{ \AA.}$ $= 2.98 \text{ \AA.}$ $= 5.96 \text{ \AA.}$ $= 1.748$ $= ca. 30 \text{ V.}$ $= -10 \text{ V.}$	Lattice: Madelung energy (<i>M</i>) = 24.2 V. Level Ni ²⁺ 3 <i>d</i> = <i>M</i> - <i>I</i> ₃ = -6 V. Level O ²⁻ 2 <i>p</i> = - <i>M</i> - <i>E</i> ₂ = -14 V. At lattice hole: Madelung energy Ni ²⁺ (<i>M'</i> _{Ni}) = 31.6 V. Madelung energy O ²⁻ (<i>M'</i> _O)* = 13.8 V. Level Ni ²⁺ 3 <i>d</i> = <i>M'</i> _{Ni} - <i>I</i> ₃ = +1 V. Level O ²⁻ 2 <i>p</i> = - <i>M'</i> _O - <i>E</i> ₂ = -3.8 V.
CuJ		
Lattice type: cubic ZnS, Shortest distance Cu ⁺ to J ⁻ = $\frac{1}{2}a\sqrt{3}$ Distance Cu ⁺ to lattice hole = $\frac{1}{2}a\sqrt{2}$ Madelung constant First ionization energy Cu (<i>I</i> ₁) Second ionization energy Cu (<i>I</i> ₂) Electron affinity J (<i>E</i>)	$a = 6.05 \text{ \AA.}$ $= 2.62 \text{ \AA.}$ $= 4.27 \text{ \AA.}$ $= 1.639$ $= 7.8 \text{ V.}$ $= 20.2 \text{ V.}$ $= -3.1 \text{ V.}$	Lattice: Madelung energy (<i>M</i>) = 9.0 V. Level Cu 4 <i>s</i> = <i>M</i> - <i>I</i> ₁ = +1.2 V. Level Cu ⁺ 3 <i>d</i> = <i>M</i> - <i>I</i> ₂ = -11.2 V. Level J ⁻ 5 <i>p</i> = - <i>M</i> - <i>E</i> = -12.1 V. At lattice hole: Madelung energy Cu ⁺ (<i>M'</i> _{Cu}) = 12.4 V. Madelung energy J ⁻ (<i>M'</i> _J) = 3.5 V. Level Cu ⁺ 3 <i>d</i> = <i>M'</i> _{Cu} - <i>I</i> ₂ = -7.8 V. Level J ⁻ 5 <i>p</i> = - <i>M'</i> _J - <i>E</i> = -6.6 V.
ZnO		
Lattice type: hexagonal ZnS, Shortest distance Zn to O Distance Zn to Zn Madelung constant First ionization energy Zn (<i>I</i> ₁) Second ionization energy Zn (<i>I</i> ₂)	$a = 3.25 \text{ \AA.}$ $c = 5.23 \text{ \AA.}$ $= 1.98 \text{ \AA.}$ $= 3.25 \text{ \AA.}$ $= 1.639$ $= 9.4 \text{ V.}$ $= 17.9 \text{ V.}$	Lattice: Madelung energy (<i>M</i>) = 23.9 V. Level Zn ⁺ 4 <i>s</i> = <i>M</i> - <i>I</i> ₂ = 6.0 V. Level Zn 4 <i>s</i> = 2 <i>M</i> - <i>I</i> ₁ - <i>I</i> ₂ † = 20.5 V. Level O ²⁻ = - <i>M</i> - <i>E</i> = -13.9 V. Lowest member $O^{3-} > -13.9 + \frac{2e^2}{r_{O^{2-}}} \dagger = > 8 \text{ V.}$ At lattice hole: Madelung energy Zn ⁺ (<i>M'</i>)§ = +13.7 V. Madelung energy Zn (<i>M''</i>) = +9.3 V. Level Zn ⁺ 4 <i>s</i> = <i>M'</i> - <i>I</i> ₂ = -4.2 V. Level Zn 4 <i>s</i> = 2 <i>M''</i> - <i>I</i> ₁ - <i>I</i> ₂ = -8.7 V.
KJ		
Lattice type: cubic NaCl, Madelung constant Distance K to J Distance K to K = $\frac{1}{2}a\sqrt{2}$ Second ionization energy K (<i>I</i> ₂)	$a = 7.05 \text{ \AA.}$ $= 1.748$ $= 3.53 \text{ \AA.}$ $= 4.99 \text{ \AA.}$ $= 31.7 \text{ V.}$	Lattice: Madelung energy (<i>M</i>) = 7.2 V. Level K ⁺ : <i>M</i> - <i>I</i> ₂ = -24.5 V. Level J ⁻ : - <i>M</i> - <i>E</i> = -10.3 V. Adjacent to failing K ⁺ Madelung energy K ⁺ (<i>M'</i>) = 10.1 V. Level K ⁺ : <i>M'</i> - <i>I</i> ₂ = -21.6 V. Madelung energy J ⁻ (<i>M''</i>) = 3.1 V. Level J ⁻ : <i>M''</i> - <i>E</i> = -6.2 V.

* For two O⁻ ions adjacent to a vacant Ni²⁺ lattice point.

† For two electrons at one Zn²⁺ lattice ion.

‡ If an electron is added to O²⁻ there are no discrete levels; the lowest member of the continuum will be at least $2e^2/r_{O^{2-}} = 22 \text{ V.}$ higher ($r_{O^{2-}} = 1.3 \text{ \AA.}$ = radius of O²⁻).

§ For two Zn⁺ ions adjacent to a vacant oxygen lattice point.

adjacent to a vacant Ni^{2+} point) amounts to ($A = \text{Madelung constant}$):

$$\frac{2A\epsilon^2}{r} + \frac{2\epsilon^2}{r\sqrt{2}} - \frac{\epsilon^2}{2r\sqrt{2}} = 24.2 + 9.8 - 2.4 = 31.6 \text{ volts}$$

The electronic level of these ions is therefore raised 7.4 volts with respect to normal lattice ions, or rather considerably less owing to several polarization effects. The other data are calculated in a similar way.

In the case of ZnO the deviation from stoichiometry causing electronic conductivity is an excess of Zn. In the analogous case of BaO it has been shown that the red BaO containing an excess of about 1 per cent Ba has a density of about 0.5 per cent less than that of normal BaO⁽¹⁹⁾. We will therefore assume in BaO and similar substances that the excess of metal is present at normal lattice points, whereas a number of oxygen lattice points is vacant, though, for the case of ZnO, the possibility cannot wholly be excluded that Zn takes interlattice points, since Zn is more polarizable than Ba, and ZnO has a different lattice type. In the case of ZnO extra electrons must be introduced and we must therefore consider the *lowest unoccupied* level in the lattice and at lattice holes. From table 2 we make the following inferences.

For NiO with oxygen excess: both in the normal lattices as well as at lattice holes the removal of electrons leads to Ni^{3+} ions and never to O^- ions.

For CuJ with iodine excess: in the normal lattice Cu^{2+} are formed; adjacent to vacant Cu^+ lattice points the highest occupied level seems to be J^- and therefore J atoms are formed; the latter conclusion is somewhat uncertain owing to the high polarizabilities of the ions involved.

For ZnO with metal excess, assuming vacant oxygen lattice points: adjacent to an absent O^{2-} ion the lowest unoccupied level is that for a Zn atom. In the regular lattice, however, an excess of electrons yields a more uniform distribution of the electrons and leads to Zn^+ ions. The formation of O^{2-} can be excluded.

For KJ with iodine excess: the electrons are always removed from J^- ions.

§ 3. MECHANISM OF CONDUCTION

We now proceed to a consideration of the mechanism of electronic conduction. The theory of electronic states in metals has been developed on the basis of the assumption that the interaction of the electrons and ions of the lattice can be approached by treating each electron as moving in the field of the ions and the average field of all other electrons. This method of approach implies that all atoms (ions) of a definite kind contain an equal number of electrons, or, since electron movement must necessarily alter the number of electrons of an atom temporarily, that local charge differences are neutralized by other electrons within a short time; in other words that the electrons are free to such an extent that they can still be considered as *not* belonging to definite atoms. If the potential barrier between the atoms (ions) of one kind is increased the probability of interchange of electrons decreases rapidly and the time lag mentioned above increases. Thus, for somewhat higher potential barriers the state of affairs is finally fundamentally different

in metallic conduction. There is a certain probability that an electron leaks through a potential barrier to a neighbouring atom, say from one Ni^{2+} to another Ni^{2+} in pure NiO. The immediate result is that in a row of Ni^{2+} ions two adjacent Ni^{2+} ions are changed into Ni^+ and Ni^{3+} . If the excess of positive charge at the Ni^{3+} ions is not sufficiently rapidly neutralized by other electrons the probability is high that the electron at the Ni^+ ions does not travel further into the lattice, but moves back, even against the force resulting from the applied electrical field, to the original atom. The theoretical treatment of the electronic movement will obviously be quite different from that in the theory of metals and must consist of a discussion of the probability of the existence and prevalence of such charge disturbances and the chance of propagating the electrons from them to other similar disturbances. In default of such a treatment we may provisionally infer that the nature of such an electronic conduction mechanism probably implies that in a certain region the conductivity will be highly sensitive to the height of the potential barriers. Substances with partially filled energy zones will therefore, according to this qualitative picture, generally be either metals or poor conductors, whereas intermediate cases will probably be rare. Substances of the latter intermediate type, i.e. semi-conductors with appreciable conductivity, will, however, be rather interesting, since one might expect their conductivities to be very sensitive to changes in the lattice spacings and thus to the situation of the bands with respect to the potential barriers, and therefore, not only to temperature, but also to external pressure, formation of solid solutions etc.

The existence of semi-conductors or insulators with partially filled energy zones, could not, indeed, be properly understood from the viewpoint of the present theory of electronic states for metals^(20, 21). A peculiar difficulty was also offered by a substance like Fe_3O_4 , for according to these views one could not immediately explain why a substance with a partially filled $3d$ band containing $5\frac{1}{2}$ electrons per Fe atom should conduct 10^{11} times as well as a substance of the same lattice type and practically identical lattice dimensions with a partially filled $3d$ band containing 5 electrons per Fe atom (γ Fe_2O_3). Similar arguments hold for the non-stoichiometric compounds. For these substances the Wilson model for extrinsic semi-conductors⁽⁴⁾, eventually the modified model of de Boer and van Geel⁽²²⁾, cannot be applied. According to this theory, semiconduction has been explained by discrete impurity levels; if energy is taken up from the thermal movement, electron transitions are assumed to occur from these levels to a normally completely empty band, or from a completely filled band to empty impurity levels. In the cases under consideration, however, this mechanism cannot help us, since the energy band ($3d$) is partially filled with electrons in the stoichiometric compounds as well as in the non-stoichiometric ones; and it cannot explain the considerable increase in the conductivity if the substance no longer contains a whole number of electrons per ion.

Our consideration given above showing that substances with partially filled energy bands must actually be expected to be poor conductors, if only the potential barriers are sufficiently high to reduce the frequency of interchange below a certain limit, which, for instance, can be of the order of the inverse of the duration of an

"excited lattice state" (in our example $\text{Ni}^+ - \text{Ni}^{3+}$), explains immediately the effect of a non-integral number of electrons per atom in a band, or, in other words, of an average structure of a cation lattice with unequally charged ions (or in part atoms) of the same element. If, for instance, in Fe_3O_4 an electron moves from a Fe^{2+} ion to a Fe^{3+} ion at an equivalent lattice point, the initial ion is transformed into Fe^{3+} and the accepting ion into Fe^{2+} . As a consequence of this reaction (indicated according to Wagner by $\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$), if only it occurs simultaneously at several points in the lattice, no fundamental change in the statistical distribution of Fe^{2+} and Fe^{3+} has occurred. The essential difference from the foregoing case is that the electronic movement does not automatically imply the appearance of a charge disturbance inhibiting further electronic transport. In a perfect Fe_3O_4 crystal the chain of electronic interchanges is only broken down at the surface of the crystals. Since after each electronic transition the energy state of the lattice is not altered (except for minor effects), the amount of energy necessary for each electron transi-

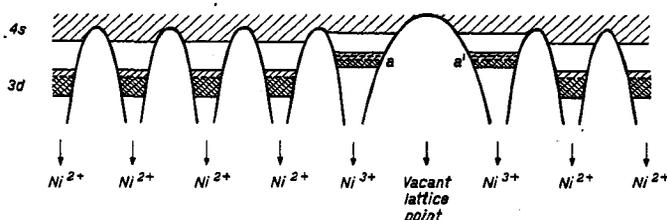


Figure 1. Schematic representation of the 3d and 4s band in a substance like NiO, containing a small amount of oxygen in excess. Section through a row of Ni^{2+} ions (110 direction) with one absent cation.

tion is very small. Such a lattice with a statistical distribution of unequally charged homonymous ions shows therefore a high conductivity and a low temperature coefficient.

Let us now consider the periodic potential field along a row of cations (in a face-centred lattice, therefore a (110) direction) in a substance with a partially filled 3d band like NiO, disturbed at one point by the absence of one cation (figure 1).^{*} At absolute zero two of the only slightly broadened levels of the Ni ions adjacent to the lattice hole (in the three-dimensional lattice there are 12 such ions), *a* and *a'*, contain one electron less than the normal lattice ions. The partially filled 3d band of the normal lattice ions does not give rise to any appreciable conduction owing to the effect of the potential barriers, as considered above. Electronic interchange takes place easily only between the 12 cations adjacent to the lattice hole sharing 10 electrons, but this does not lead to any transport of electricity in an electric field. The 4s band especially is strongly broadened by the lattice, but the bands are still separated by a considerable forbidden energy region. Actually pure NiO does not absorb strongly in the region of visible light; its colour is a light yellowish green.

^{*} Strictly speaking also the second nearest neighbours, etc. of a lattice hole have slightly raised levels, and also the potential barriers are slightly changed. The schematic picture of figures 1-3, however, is sufficient for our purpose.

The forbidden region can therefore be estimated to be somewhat less than 3 volts. Upon introduction of a small excess of oxygen, however, the colour turns into black, which is probably connected with transitions from the raised levels a , a' into the empty $4s$ zone of the lattice. The introduction of an excess of oxygen, i.e. of a number of levels a , a' (being partially Ni^{3+} ions, namely $\frac{1}{3}$ of them), simultaneously increases the conductivity, of which the mechanism can now be understood in the following way. If the temperature is above absolute zero there is a certain probability that a normal lattice Ni^{2+} ion gives off its electron to one of the Ni^{3+} ions adjacent to the lattice hole, for which transition an amount of energy must be supplied from the thermal movements in order to bring the electron into the higher levels a , a' . The result is that a row of normal lattice ions contains a Ni^{3+} ion of the same energy level as the Ni^{2+} ions, and conditions as considered for the case of Fe_3O_4 are created. Hence a chain of transitions $\text{Ni}^{2+} + \text{Ni}^{3+} \rightarrow \text{Ni}^{3+} + \text{Ni}^{2+}$ sets in, which, in the presence of an electric field, leads to electronic conduction. If during such a chain of transitions the electronic deficit propagated through the lattice meets a lattice hole, i.e. when a Ni^{2+} ion in the neighbourhood of such a hole is converted into a Ni^{3+} , there

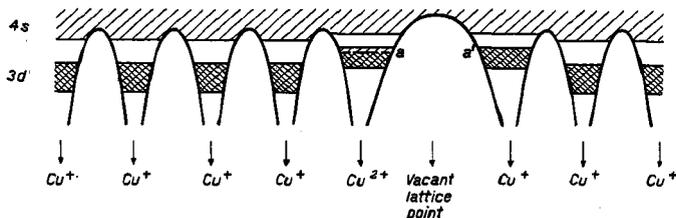


Figure 2. Schematic representation of the $3d$ and $4s$ band in a substance like Cu_2O , containing a small amount of oxygen in excess. Section through a row of Cu^+ ions with one absent cation.

is a large probability that an electron of a level a (a') falls back to this ion, and the chain of transitions is broken down; every new chain must start again with a jump of an electron to a non-occupied level of a Ni^{3+} ion adjacent to a lattice hole. In this way an equilibrium is established, and the total number of Ni^{3+} ions at normal lattice points, and therefore the conductivity, depends on the temperature according to a Boltzmann partition law.

In the case of Cu_2O or CuJ the picture is somewhat different owing to the fact that here the band of $3d$ electrons is completely occupied. Figure 2 shows again the case of a row of Cu^+ ions and one absent cation. In this case one of the cations directly surrounding the lattice hole (in figure 2 there are only two, again represented by somewhat raised levels a and a') contains one electron less (Cu^{2+} ion). The red colour of Cu_2O indicates that the Cu^+ $3s$ and the Cu $4s$ zone are separated by a forbidden zone of about 2 volts (the spectral photoelectric region, according to this transition, lies at about $630 \text{ m}\mu$, corresponding to about 2 volts); the "centre" of the latter lies 12.4 volts higher than that of the former (§ 2, table 2). At absolute zero no conduction is possible, since the $3d$ band is completely occupied and the $4s$ zone is entirely empty. At higher temperature three conductivity mechanisms are possible:

- (1) Electron transitions from 3d into 4s.
- (2) Electron transitions from levels a, a' etc. into the 4s zone.
- (3) Electron transitions from the 3d band into the level a .

(1) leads to electronic movement of an electron in 4s and of an electron hole in 3d, the former predominating; (2) leads only to the former, whereas electron transitions (3) imply defect conductivity in 3d. According to measurements⁽¹⁸⁾ of the Hall constant and measurements of the thermo-e.m.f.⁽¹⁷⁾ of Cu_2O containing a small excess of oxygen this substance shows defect conductivity and therefore obviously the third mechanism prevails. If, however, the Cu_2O is heated in a high vacuum, the substance thus obtained, which will be now close to the stoichiometric composition, is still an electron hole conductor at lower temperatures, but above 500° it shows a negative Hall constant. Obviously the number of Cu^{2+} ions at levels a etc. is so small now that at higher temperatures mechanisms (1) and (2), owing to their larger temperature coefficient, will finally predominate over (3), whereas at lower temperatures the activation energy of (1) and (2) are too high to yield an important conductivity. It should be pointed out that the number of lattice holes of the type of figure 2 will be larger than the number of Cu^{2+} ions at such lattice holes, owing to thermal lattice deviations at the temperature at which the crystal was formed (Schottky-Fehlstellen); all such levels at lattice holes can contribute to mechanism (2), whereas only an unoccupied level a can contribute to mechanism (3). In pure Cu_2O all copper ions are Cu^+ ions and therefore only (1) and (2) should be possible.

With increasing amount of excess oxygen ions the mutual influence of the various lattice holes and of the ions with higher charge lowers the levels a, a' etc. Owing to the statistical distribution of these lattice holes and higher charged ions the levels do not have the same height throughout, but as a whole they are all lowered more or less, since with increasing number of such vacant lattice points the direct environment of ions adjacent to the hole becomes increasingly more symmetrical and their average height above the 3d band is therefore lowered continually. The lowest levels give the largest contributions to mechanism (3). Actually we find that the activation energy as derived from the temperature coefficient of the conductivity of Cu_2O decreases from 0.72 volts to 0.13 volts with increasing oxygen content⁽²³⁾. In the case of $\text{CuJ}^{(24)}$ a sufficient excess of iodine (corresponding to $\text{Cu}_{0.995}\text{J}$) leads to a negative temperature coefficient, indicating that in that case the lowest levels a, a' etc. do not rise any more above the highest members of the lattice 3d band.

Photoconductivity occurs with Cu_2O and CuJ , not with NiO (independently of deviations from stoichiometry). With the aid of the models given above we may make the tentative hypothesis that photoconductivity, for equal relative positions of the bands with respect to the potential barriers, will be much greater in the case of figure 2 than of figure 1. This can be seen in the following way. Transitions from the lattice 3d band into the levels a, a' etc. need not be considered, since as optical transitions they are not allowed. Transitions (1) and (2) are permitted; both transitions can be deduced from the spectral distribution of photoconductivity in the case of Cu_2O with an excess of oxygen, a normal band with a maximum of $630 \text{ m}\mu$. and a band connected with the oxygen excess at about $1700 \text{ m}\mu$.⁽²⁵⁾ In the case of a

substance with a completely filled $3d$ band a photoelectrically released electron, moving through the lattice under the influence of an applied field, for instance from a Cu^+ ion adjacent to a vacant lattice point, can only fall back to a lower level when it encounters an electronic hole. In the case of NiO , however, the wandering electron can fall back at any time to the $3d$ band, since sufficient empty electronic states are available. Also in this $3d$ band the additional electron can travel further through the lattice, until it reaches an electronic hole (Ni^{2+} ion), but in this band its mobility is considerably smaller than in the $4s$ band, owing to the higher potential barriers to be penetrated; hence only the electrons in the $4s$ band should make a practical contribution to the photoconduction. As a consequence of the much smaller average path length the photoconductivity in NiO will then be correspondingly smaller for otherwise equal conditions.

Another possibility, explaining the photoconductivity of these substances with completely filled bands, which cannot wholly be excluded, is suggested by our remark in § 2 that in CuJ the electron deficit at the lattice holes is perhaps not present

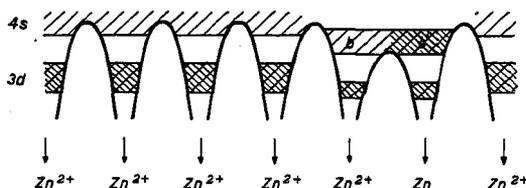


Figure 3. Schematic representation of the $3d$ and $4s$ band in a substance like ZnO , containing a small amount of Zn in excess. Section through a row of Zn^{2+} ions touching a lattice hole due to an absent oxygen ion.

at the copper ions (producing Cu^{2+}), but at the J^- ions (thus converted into J atoms). If the latter corresponds to the actual state of affairs for CuJ , the transition of an electron from the Cu^+ $3d$ band into the $5p$ level of those J atoms takes the place of transition (3), and this is permitted as an optical transition. In that case photoconduction can be explained as conduction in the Cu^+ $3d$ band as a consequence of optically released electrons according to the (modified) transition (3). This might be the mechanism for all these substances, if it could be proved to be a general rule that with cations with a complete electronic group or subgroup the electron deficit at the lattice holes is preferably located at the anions. For this a more careful calculation of the electronic levels, which must be reserved to the future, would be necessary.

For sake of completeness we also give, figure 3, the situation of the levels for ZnO containing a small amount of metal in excess, on the assumption of vacant oxygen lattice points. Electronic conduction occurs after thermal excitation of an electron from the occupied $4s$ level b' (Zn atom adjacent to a vacant oxygen lattice point) into the $4s$ band, converting a normal lattice ion into Zn^+ . Photoconductivity can occur by excitation from $3d$ either into a level b , b' etc. or into the normal $4s$ band.

Finally it should be pointed out that several features of these semiconductors could be understood with the aid of a model using Smekal's structure-sensitive lattice flaws⁽²⁶⁾. The above picture, however, enables a more complete description of the phenomena and seems preferable in the light of recent results on lattices with vacant lattice points^(27,28) and on the nature of thermal lattice deviations by Wagner and Schottky.*

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* A similar treatment of the colour centres in the alkali halides has been given by de Boer⁽²⁹⁾.