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## Abstract

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# PHOTOELECTRIC EMISSION FROM THE SURFACE OF

## $Cr_2O_3$, NiO, ZnO

*(Presented by Academician A. N. Terenin on 20 III 1961)*

A comparison of the electrical, optical, magnetic, and other characteristics of transition-metal oxides, carried out by Mottin (?) ($^1$), shows that the *d*-electrons in chromium oxide and nickel monoxide do not form bands, and that the cations of these metals may, to a good approximation, be regarded as isolated. Although at present the structure of the energy states of these oxides has been little studied, the data collected in that work indicate that the *d*-levels of the transition-metal cations are located considerably above the oxygen *p*-levels. The latter form a broad filled band. This mutual arrangement of the energy states of the *d*- and *p*-electrons makes the indicated transition-metal oxides very convenient objects for investigating photoemission caused by *d*-electrons, which may be regarded as localized in the vicinity of the corresponding cation.

In the present work an investigation was made of the distribution of photoelectrons by kinetic energies from the oxides of chromium, nickel, and zinc by the retarding-field method in a spherical condenser. The measurements were carried out on an apparatus that had earlier been used for studying photoemission from solid layers of organic dyes ($^2$).

The chromium oxide samples studied were layers of finely dispersed powders obtained by calcination of a thin layer of ammonium bichromate ($^3$), deposited on nickel disks 12 mm in diameter from a suspension in ethanol or water. Samples of nickel monoxide were prepared in an analogous manner from a finely dispersed powder (commercial preparation). Layers of nickel monoxide obtained by oxidation of nickel disks in air were also studied. Zinc oxide samples were prepared by depositing a suspension of ZnO powders in ethanol and water. Oxide powders obtained from zinc oxalate, by burning pure zinc, and from a commercial preparation of the grade "for luminophores" were studied. Layers obtained by direct sublimation of zinc oxide onto nickel disks during the burning of zinc in air were also investigated. Before the measurements all samples were heated under pumping directly in the spherical condenser to a temperature of 200–250° for nickel monoxide and to 350–400° for the oxides of chromium and zinc for 2-3 hours. Heating was carried out with the aid of a small furnace fastened to the rear side of the photocathode. The indicated conditioning conditions could

Figure 1

Figure 1: Figure 1

not completely clean the surface of the sample, and therefore the cited values of the photoelectric work function may differ from the true ones. Indeed, in the study of the external photoeffect from transition-metal oxides in investigations carried out earlier ($^4$), it was shown that upon adsorption of simple gases and organic vapors the threshold of photoelectric emission can shift appreciably—by as much as 1 eV. However, as a result of such conditioning the gases adsorbed on the surface of the samples should come into equilibrium with the residual gases in the volume, and the magnitude of the photoelectric work function will remain constant during the experiment. It should be noted that adsorbed gases cannot appreciably change the character of the distribution of photoelectrons over energies.

As a result of investigating samples of different origin and prepared by different methods, it was found that the character of the distribution of photoelectrons by energy changes only slightly. This indicates that photoemission is due to the oxides' own electrons, and not to the content of impurities in them.

Figure 1 presents graphs of the distribution of photoelectrons by kinetic energies from chromium oxide for photon energies from 7.7 to 11.2 eV, obtained by graphical differentiation of the corresponding volt-ampere curves.

Fig. 1. Distribution of photoelectrons by energy for a chromium oxide layer at different light-quantum energies: 1—7.7 eV; 2—8.2 eV; 3—8.5 eV; 4—9.1 eV; 5—9.9 eV; 6—11.2 eV

The graphs for different photon energies are reduced to the same intensity of the incident photon beam. As long as the energy of the photoelectrons does not exceed 2 eV, the curves shown in the figure have one maximum, which broadens toward higher energies by the amount of the increase in the energy of the light quanta. At a photon energy of 8.2 eV, in the region of the very lowest photoelectron energies, a new maximum is clearly observed, which, with a further increase in the quantum energy, like the first maximum, broadens toward higher kinetic energies. On the curves corresponding to photon energies of 9.9 and 11.2 eV, the appearance of a new maximum is observed, the beginning of whose rise lies in the region of electron energies 3.2-3.3 eV lower than those of the fastest electrons. It should be noted that at a photon energy of 11.2 eV the number of electrons with low energies (0-0.5 eV) is sharply reduced.

Although chromium oxide has absorption bands corresponding to energies of 2.1 and 2.6 eV, the described course of the experimental electron energy-distribution curves cannot be explained by discrete losses of kinetic energy by the photoelectrons during their motion toward the surface of the crystal. Between the observed optical absorption band and the appearance of the third group of electrons there is a difference of more than 0.5 eV, whereas the error of our ex-

Fig. 2. Energy distribution of photoelectrons for a nickel oxide layer at different photon energies: 1—6.3 eV; 2—6.6 eV; 3—7.1 eV; 4—8.5 eV; 5—9.8 eV

Figure 2: Fig. 2. Energy distribution of photoelectrons for a nickel oxide layer at different photon energies: 1—6.3 eV; 2—6.6 eV; 3—7.1 eV; 4—8.5 eV; 5—9.8 eV

periments should not exceed 0.2-0.3 eV. Further, if a discrete loss of energy by fast photoelectrons were observed, the appearance of intense groups of slow electrons would be accompanied by a sharp decrease in the number of fast electrons, which is not observed experimentally. On the contrary, with increasing photon energy there is a monotonic increase in the number of fast electrons. Finally, in the case of discrete losses by fast electrons, one should observe a decrease or a slowing of the growth of the quantum yield of photoemission with increasing photon energy. Experimentally the opposite result is observed—when groups of slow photoelectrons appear, the photoemission yield increases more sharply.

A more probable explanation of the mechanism of the photoeffect from the surface of chromium oxide should be considered either the ejection of electrons located at···

various energy levels, or the tearing of electrons from one level with simultaneous excitation of the resulting quadruply charged chromium positive ion to lower excited levels. At present there are no data for a rigorous choice of the mechanism of the photoeffect from the two latter processes cited; however, the detachment of an electron with excitation of the resulting quadruply charged ion seems to us the more substantiated.

Fig. 2. Energy distribution of photoelectrons for a nickel oxide layer at different photon energies: 1—6.3 eV; 2—6.6 eV; 3—7.1 eV; 4—8.5 eV; 5—9.8 eV

In support of this, let us compare the positions of the terms of Cr$^{4+}$ (5) with the appearance of new maxima on the electron energy-distribution curves.* In the optical absorption spectrum of chromium oxide there are two distinct bands with maxima at 16 800 and 21 300 cm$^{-1}$, while Cr$^{3+}$, relative to the normal level, has a number of terms near 15 000 and 21 000 cm$^{-1}$. There is no reason to suppose that this good agreement will not also hold for the Cr$^{4+}$ ion, which relative to the normal level has a number of terms with energies 1.85-1.99 eV and one term with energies 2.9 and 3.15 eV. Taking into account that in our experiments the levels with energies 2.9 and 3.15 eV may be forbidden, one should expect two slow groups of electrons with kinetic energies 2 and 3 eV less than the energy of the fastest electrons, which is indeed observed experimentally. We note that the character of the electron energy-distribution curves in the case of chromium oxide strongly resembles the corresponding curves for photoionization electrons, where the appearance of new maxima is explained in an analogous way.

The structure of the levels of nickel oxide is analogous to the structure of the levels of chromium oxide (1); the *d*-electrons of Ni$^{2+}$ are likewise, and even to a greater extent, localized. However, the terms of nickel ions and the absorption

Fig. 3. Energy-distribution curves of photoelectrons for zinc oxide, normalized to the saturation current: 1—7.7 eV; 2—8.1 eV; 3—8.5 eV; 4—9.1 eV; 5—9.5 eV; 6—10.2 eV; 7—11.2 eV

Figure 3: Fig. 3. Energy-distribution curves of photoelectrons for zinc oxide, normalized to the saturation current: 1—7.7 eV; 2—8.1 eV; 3—8.5 eV; 4—9.1 eV; 5—9.5 eV; 6—10.2 eV; 7—11.2 eV

bands of nickel oxide (6) are situated closer together. This makes the electron energy-distribution curves in the case of NiO analogous to those of $Cr_2O_3$, but because of the smaller energy separations between levels the maxima are less distinct. The data obtained for nickel oxide are shown in Fig. 2. They show that for nickel oxide the mechanism of the external photoeffect must be the same as in the case of chromium oxide.

The experimental graphs of the energy distribution of photoelectrons from the surface of zinc oxide, for quantum energies from 7.7 to 11.2 eV, normalized to the saturation-current value, are presented in Fig. 3. The character of the electron energy distribution is entirely different from the case of the transition-metal oxides. Most of the photoelectrons at photon energies below 9.5-10.0 eV have a very small kinetic energy, and only with a further increase in photon energy does the peak in the electron energy distribution broaden noticeably toward higher kinetic energies. Such curves are typical for a number of oxides, photoeffect of which is due to the ejection of valence electrons forming a broad filled band (see, for example, (7)).

The large number of slow electrons in the case of photoemission from zinc oxide can be explained by two reasons: the presence of a broad valence band (of width on the order of 3-4 eV (8)) makes possible the ejection of electrons whose work functions differ by 3-4 eV, and the presence in zinc oxide of excess zinc atoms, upon collision with which scattering of the energy of the photoelectrons occurs as they move toward the surface of the crystal. This explanation is confirmed by the following experimental data. Broadening of the peak on the electron energy-distribution curves begins when the maximum energy of the photoelectrons reaches 3.5-4.0 eV, i.e., after the magnitude of the incident light quantum becomes greater than the energy difference between the vacuum level and the bottom of the filled band, taking its width to be 3-4 eV.

**Fig. 3.** Energy-distribution curves of photoelectrons for zinc oxide, normalized to the saturation current: 1—7.7 eV; 2—8.1 eV; 3—8.5 eV; 4—9.1 eV; 5—9.5 eV; 6—10.2 eV; 7—11.2 eV

The study of the energy spectra of photoelectrons from various zinc oxide sam-

* Although the positions of the terms are given for the ion in the gas phase, such a comparison seems justified because of the weak interaction of the electrons with the electrons of neighboring ions.

ples, carried out in the present work, shows that scattering of the kinetic energy of the photoelectrons is considerably greater in those samples that contain a larger amount of excess zinc.

The experimental data presented above indicate that the study of the distribution of photoemission electrons makes it possible to obtain information not only on the position of the occupied energy states, but also on the nature of these states.

The photoelectric work functions of chromium oxide, nickel monoxide, and zinc oxide, from the data we obtained, have values of 5.9, 5.3, and 6.3 eV, respectively, and the positions of the Fermi level relative to the vacuum level are 5.9, 6.0, and 4.6 eV, respectively. As noted above, these values may differ somewhat from the true values, since the conditioning conditions could not ensure complete cleaning of the surfaces of the samples from adsorbed gases.

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