PHYSICS

Corresponding Member of the Academy of Sciences of the USSR E. F. GROSS and CHANG GUAN-YIN

1962

SovietRxiv

Abstract

Full Text

PHYSICS

Corresponding Member of the Academy of Sciences of the USSR E. F. GROSS and CHANG GUAN-YIN

THE EXCITON REFLECTION SPECTRUM OF A CUPROUS OXIDE CRYSTAL IN THE ULTRAVIOLET REGION

As is known, in the absorption spectrum of a cuprous oxide crystal two groups of lines are observed—the yellow and the green—in the form of two hydrogen-like series. At present, after a number of experimental works ($^{1-4,\ 8}$) and theoretical investigations by P. Elliott, A. G. Zhilich, and S. A. Moskalenko ($^{5-7}$), and especially after Elliott' s recent work (^{5}), there is no doubt that the yellow and green hydrogen-like series of lines in Cu_2O belong to the exciton. Recent studies have shown that the spectrum of a cuprous oxide crystal is not limited to the yellow and green groups of lines, but has a more complex character.

As was established in our laboratory by I. Pastrnyak (^{8}), using the method of reflection of light from the surface of a Cu_2O crystal, distinct reflection structures are observed in the blue and violet parts of the spectrum in the regions near $\lambda = 4880$ Å and $\lambda = 4635$ Å. This indicated that strong absorption of light in these regions must occur in Cu_2O crystals.

We undertook a careful investigation of the facts discovered by Pastrnyak, and not only confirmed his results but also obtained new data. By applying in this work an improved method for studying the reflection spectra of crystals, we found new reflection lines, as well as absorption lines (^{9}), in the blue and violet regions of the spectrum. These results leave no doubt that the blue and violet series of lines observed by us belong to the excitons of the Cu_2O crystal and are well explained by the band schemes of Cu_2O proposed by Elliott (^{5}), Zhilich (^{6}), and Moskalenko (^{7}).

Our experimental investigations show the complexity of the band scheme of the Cu_2O crystal and the existence of exciton spectra deep within the fundamental absorption band, associated with exciton levels near the higher-lying conduction bands. The question arises whether the complexity of the Cu_2O spectrum is limited to the already observed series of lines, or whether one must assume the existence of new, as yet unknown regions of exciton spectra in Cu_2O. The latter seemed natural to us, in particular the possibility of exciton transitions associated with spectra in the ultraviolet region.

This assumption is justified by the following considerations. First, the existing

Fig. 2. Microphotogram of the reflection spectrum from a Cu_2O single crystal in the ultraviolet region. a —microphotogram of the reflection spectrum of a Cu_2O crystal with maxima λ_1, λ_2, and λ_3. b —microphotogram of the emission spectrum of a hydrogen lamp in the same spectral region

Figure 1: Fig. 2. Microphotogram of the reflection spectrum from a Cu_2O single crystal in the ultraviolet region. a —microphotogram of the reflection spectrum of a Cu_2O crystal with maxima λ_1, λ_2, and λ_3. b —microphotogram of the emission spectrum of a hydrogen lamp in the same spectral region

theories of the band scheme of the cuprous oxide crystal by Elliott (5), Zhilich (6), and Moskalenko (7) assume the existence of lower-lying valence bands and higher-lying conduction bands, in addition to the bands corresponding to the results of Pastrnyak (8) and to our experiments (9). Second, this assumption is confirmed experimentally by photoelectric phenomena in Cu_2O.

Already in the early works of A. Pfund (10) and A. V. Ioffe and A. F. Ioffe (11), it was indicated that the photoconductivity of a cuprous oxide crystal in the ultraviolet region of the spectrum has a maximum at 2800 Å at room temperature. It is natural to regard this work as experimental evidence of the complexity of the band structure of the cuprous oxide crystal and of the possibility

existence of an intense discrete absorption band in the ultraviolet region of the spectrum. However, direct optical observation of the absorption of a cuprous oxide crystal in this spectral region has still not been carried out, owing to difficulties caused by the large absorption coefficient in this region. Here, however, the reflection method can be applied, making it possible to reveal the structure of the discrete bands in this spectral region.

We undertook an investigation of the reflection spectrum of a Cu_2O crystal in the ultraviolet region of the spectrum. In a previous work (9), we applied an improved reflection method to investigate the structure

Fig. 2. Microphotogram of the reflection spectrum from a Cu_2O single crystal in the ultraviolet region. **a** —microphotogram of the reflection spectrum of a Cu_2O crystal with maxima λ_1, λ_2, and λ_3. **b** —microphotogram of the emission spectrum of a hydrogen lamp in the same spectral region.

of exciton lines of a cuprous oxide crystal in the blue and violet regions of the spectrum. The method is based on the fact that the most contrasted structures of the reflection bands appear only in the *p*-component of the reflection at angles of incidence close to Brewster' s angle. In the present work the same method was used in combination with double reflection.

The investigation of the reflection spectra of Cu_2O crystals in the ultraviolet region was carried out by us on a quartz spectrograph Q-12 made by C. Zeiss. A hydrogen lamp VU-1 served as the light source. In Fig. 1b (see insert,

Fig. 3. Reflection curve from a Cu2O single crystal in the ultraviolet region at $t = 20°\text{C}$ with reflection maxima λ_1'—λ_5'

Figure 2: Fig. 3. Reflection curve from a Cu2O single crystal in the ultraviolet region at $t = 20°\text{C}$ with reflection maxima λ_1'—λ_5'

p. 1313) the spectrum of this lamp in the region under study is shown, and in Fig. 2b its microphotogram. As is seen from the spectrogram, the lamp spectrum is continuous, and its intensity decreases toward shorter wavelengths. In the region with wavelengths $\lambda > 3500$ Å, the lamp spectrum, as is seen from Fig. 1b, contains several emission lines, which, however, did not interfere with our measurements.

The cuprous oxide crystals studied were single crystals whose surfaces had been etched with nitric acid. The ultraviolet reflection spectra of Cu_2O were investigated at the temperature of liquid nitrogen (77°K) in polarized light in the p-component, at an angle of incidence of 70°. In Fig. 1a (see insert, p. 1313) the reflection spectrum of a Cu_2O crystal obtained by us is presented, and in Fig. 2a its microphotogram. In Figs. 1a and 2a three reflection maxima are visible at $\lambda_1 = 3410$ Å (3.64 eV); $\lambda_2 = 2860$ Å (4.33 eV); $\lambda_3 = 2620$ Å (4.73 eV). As is seen from the figure, the maxima in the ultraviolet are broader than in the blue and violet regions of the spectrum.

Under the experimental conditions described, we were unable to obtain a reflection spectrum in the shorter-wavelength region. To extend the investigated region into the short-wavelength part of the spectrum, we carried out reflection measurements on an SF-4 spectrophotometer at room temperature. Fig. 3 shows the reflection curve from 4000 to 2000 Å, taken at an angle of incidence of 30°. Five reflection maxima were obtained at $\lambda_1' = 3590$ Å (3.45 eV); $\lambda_2' = 2920$ Å (4.26 eV); $\lambda_3' = 2560$ Å (4.84 eV); $\lambda_4' = 2330$ Å (5.32 eV); $\lambda_5' = 2200$ Å (5.63 eV). Comparison of the positions of the first two reflection bands λ_1' and λ_2' with λ_1 and λ_2 (Fig. 1) shows that, with increasing temperature, the bands shift to the long-wavelength side.

It may be assumed that, of all the observed bands, only the reflection band λ_2 coincides with the photoconductivity maximum indicated in Refs. (10, 11).

The large width of the Cu_2O reflection maxima in the ultraviolet region is noteworthy. An estimate of the half-width of the ultraviolet reflection bands λ_1, λ_2, and λ_3 gives: 690, 550, and 200 cm^{-1}. The reflection at the maxima is large, which indicates a very high absorption coefficient in these bands, apparently considerably larger than for the blue and violet exciton series. This leaves no doubt that we are dealing here with the fundamental lattice of Cu_2O.

Fig. 3. Reflection curve from a Cu_2O single crystal in the ultraviolet region at $t = 20°\text{C}$ with reflection maxima λ_1'—λ_5'

The existence of ultraviolet reflection bands, in our view, cannot be associated with those zones of Cu_2O that determine absorption in the yellow, green, blue, and violet exciton series of lines. We suppose that other zones of Cu_2O play a role in their formation.

We attribute the origin of the ultraviolet bands to excitons in Cu_2O and associate their formation with the excitation of electrons from deeper valence subbands to exciton levels located near higher conduction subbands. The large absorption coefficients in the bands show that these exciton bands correspond to allowed transitions in the band scheme of Cu_2O, and each observed band is apparently the first member of the corresponding exciton series. In favor of the exciton, rather than band, origin of the ultraviolet bands are their discreteness and relatively small width. The width of the ultraviolet bands exceeds the width of the first member of the blue exciton series by only 1.5–4 times.

A clear regularity is observed in the width of the lines of the Cu_2O exciton series—their regular broadening as one moves deeper into the continuous band of "fundamental" absorption. The width of the exciton lines (for definiteness estimated from the first members of the series) gradually increases from the yellow series to the green, blue, violet, and finally to the ultraviolet. We believe that the strong broadening of the exciton lines located deep in the fundamental band is associated with the processes of autoionization of excitons and with a decrease in their lifetimes in the crystal.

Physicotechnical Institute
named after A. F. Ioffe
Academy of Sciences of the USSR

Received
6 II 1962

REFERENCES

1. E. F. Gross, K. A. Karyev, DAN, 84, 471 (1952); E. F. Gross, B. P. Zakharchenya, DAN, 90, 745 (1953); ZhTF, 27, 1940 (1957).
2. M. Hayashi, K. Katsuki, J. Phys. Soc. Japan, 7, 599 (1952).
3. I. S. Gorban, Opt. i spektroskopiya, 9, 759 (1960).
4. S. Nikitine, J. B. Grun, M. Sieskind, J. Phys. Chem. Solids, 17, 292 (1961); J. B. Grun, M. Sieskind, S. Nikitine, J. Phys. Rad., 22, 176 (1961).
5. R. J. Elliott, Phys. Rev., 108, 1384 (1957); 124, 340 (1961).
6. A. G. Zhilich, Vestn. LGU, No. 22, 5 (1959); No. 10, 5 (1960).

7. S. A. Moskalenko, Fiz. tverd. tela, 2, 1755 (1960).
8. I. Pastrnyak, Dissertation, L., 1959; Fiz. tverd. tela, 3, 869 (1961).
9. E. F. Gross, Chzhan Guan-nin, Fiz. tverd. tela, 4, 261 (1962).
10. A. H. Pfund, Phys. Rev., 7, 289 (1916).
11. A. F. Ioffe, A. F. Ioffe, ZhETF, 6, 737 (1936); Phys. Zs. Sow. Union, 11, 241 (1937).

Note: Figure translations are in progress. See original paper for figures.