Corresponding Member of the Academy of Sciences of the USSR E. F. GROSS, CHZHAN GUAN-IN, L. E. SOLOV’ EV

1962

SovietRxiv

Abstract

Full Text

Corresponding Member of the Academy of Sciences of the USSR E. F. GROSS, CHZHAN GUAN-IN, L. E. SOLOV' EV

THE ABSORPTION SPECTRUM IN THE LIGHT-BLUE AND BLUE REGIONS OF THE SPECTRUM AND DEFORMATION EFFECTS IN THIN CUPROUS OXIDE SAMPLES

In work (^{1}) the reflection spectrum of a cuprous oxide single crystal was investigated in the light-blue and blue regions of the spectrum, and preliminary data on its absorption spectrum were also reported. In these regions two groups of exciton lines were found—the light-blue and the blue. Absorption in polycrystalline cuprous oxide films was also studied in several works (^{2}-^{4}). Of these, only in work (^{2}) were distinct absorption structures observed; in the others no absorption peaks were observed. The two reflection peaks in the light-blue and blue regions of the spectrum indicated in work (^{2}) had already been found earlier by I. Pastrnyak (^{5}).

In Fig. 1 the positions of the exciton lines and their relative intensities found in works (^{1}, ^{2}) and in the present work are compared schematically. From a comparison of these data the following discrepancy should be noted: 1) The reflection and absorption data in works (^{1}, ^{2}) agree neither in the number of intense lines nor in their positions. 2) In the absorption spectra in works (^{1}, ^{2}), although similar patterns are present, the positions of the lines do not agree.

In work (^{1}) it was suggested that the more complex pattern observed in the absorption spectrum, as compared with the reflection spectrum, is caused by stress effects in the Cu_2O samples due to their being cemented to substrates, whereas reflection was observed on uncemented thick samples. If each reflection line is assumed to be split almost symmetrically by deformation into two lines, then the contradiction between the reflection and absorption data can be explained. The aim of the present work is to test this supposition and to discuss the influence of the stress effect in thin samples on the reflection and absorption spectra.

Absorption spectrum. Observation of the absorption spectrum was carried out on an ISP-51 spectrograph with a camera of $f = 800$ mm at temperatures of 4.2 and 77.3° K. Figure 2a shows the absorption spectrum and its microphotogram for one of the thin cemented cuprous oxide single crystals of thickness approximately 1μ. In the light-blue region of the spectrum two intense absorption lines were observed, $\lambda_1^{(r)'} = 4817$ Å and $\lambda_1^{(r)''} = 4777$ Å, and two weak absorption lines at $\lambda_2^{(r)'} = 4740$ Å and $\lambda_2^{(r)''} = 4724$ Å. It should be noted that the mean position of $\lambda_1^{(r)'}$ and $\lambda_1^{(r)''}$ and the mean position of $\lambda_2^{(r)'}$ and $\lambda_2^{(r)''}$, within the limits of measurement error, respectively coincide with the positions of the reflection bands indicated by arrows in Fig. 2a.

Figure 2b shows a microphotogram of the absorption spectrum of two polycrystalline cuprous oxide films at $T = 77.3°$ K. On these films four intense lines were observed, the positions of which in the spectrum differ somewhat for the two films.

As is known, a crystal cemented or fused to a substrate is subjected to stress upon cooling. However, the magnitude of the stress in the crystal depends on its thickness. For a thick crystal the stress exists only in a thin layer adjacent to the substrate. For a thin crystal, however, the stress is distributed throughout the entire volume of the crystal. This circumstance determines the dependence of the deformation of the crystal on its thickness. If the splitting of the absorption band is caused by deformation, then the thinner the crystal, the greater the splitting.

Reflection spectra. We observed reflection from the surfaces of crystals of two specimens prepared from cuprous-oxide single crystals: one in the form of a wedge, the other in the form of a plate. Both specimens were glued to a quartz substrate. The surfaces of the crystalline plates were preliminarily etched with nitric acid. Figure 3 shows their reflection spectrum at $T = 4.2°$K. The upper part of the spectrum corresponds to reflection from the wedge-shaped single crystal, whose thickness decreases along the height of the spectrum. The lower part of the spectrum corresponds to reflection from a single-crystal plate 10–15 μ thick. Here the reflection lines $\lambda_1^{(r)}$ and $\lambda_1^{(c)}$ do not split, and their positions coincide with the data for reflection from the surface of free single crystals not glued to a substrate (see Fig. 1). In the upper part of the spectrum (the wedge spectrum), $\lambda_1^{(r)}$ and $\lambda_1^{(c)}$ split symmetrically into two lines, $\lambda_1^{(r)'}$ and $\lambda_1^{(r)''}$, and $\lambda_1^{(c)'}$ and $\lambda_1^{(c)''}$, respectively, the magnitude of the splitting increasing as the wedge thickness decreases. These results convincingly show that the observed reflection (absorption) lines $\lambda_1^{(r)'}$ and $\lambda_1^{(r)''}$ are two components of the splitting of the reflection (absorption) line $\lambda_1^{(r)}$, while the lines $\lambda_1^{(c)'}$ and $\lambda_1^{(c)''}$ are components of the line $\lambda_1^{(c)}$. In absorption we observed $\lambda_2^{(r)'}$ and $\lambda_2^{(r)''}$ (Fig. 2a), and the mean value of their positions in the absorption spectrum agrees well with the position of the line $\lambda_2^{(r)}$ obtained from the reflection spectrum. Thus, there are grounds to believe that the absorption lines $\lambda_2^{(r)'}$ and $\lambda_2^{(r)''}$ are two components of the splitting of the line $\lambda_2^{(r)}$.

Fig. 1. Diagram of the absorption and reflection spectra of Cu_2O in the blue-violet region. a—according to the data of Ref. (1), —according to the data of Ref. (2), , ,—according to the data of the present work (see Fig. 2).

The experiments described above show that, in thin glued crystals of Cu_2O,

Fig. 1. Diagram of the absorption and reflection spectra of Cu_2O in the blue-violet region. *a*—according to the data of Ref. (1), —according to the data of Ref. (2), , , —according to the data of the present work (see Fig. 2)

Figure 1: Fig. 1. Diagram of the absorption and reflection spectra of Cu_2O in the blue-violet region. *a*—according to the data of Ref. (1), —according to the data of Ref. (2), , , —according to the data of the present work (see Fig. 2)

Figure 2

Figure 2: Figure 2

each absorption line, as a result of deformation, splits into two lines. A similar phenomenon should probably occur, to an even greater degree, in thin Cu_2O crystals soldered to a glass substrate. With a large deformation the splitting may also be asymmetric. Thus, apparently, all the observed discrepancies between the absorption and reflection data can be explained.

In the case of one thin glued single crystal approximately 5 μ thick, we succeeded in observing the polarization of the reflection lines $\lambda_1^{(r)'}$, $\lambda_1^{(r)''}$, $\lambda_1^{(c)'}$, and $\lambda_1^{(c)''}$. It turned out that, for a thin glued single crystal, the reflection lines $\lambda_1^{(r)}$ and $\lambda_1^{(c)}$ each split into two mutually perpendicular polarized lines. The polarized splitting of the lines under deformation that we observed is in good agreement with the data of speci-

Fig. 2. *a* —absorption spectrum of a thin Cu_2O single crystal and its microphotogram; *b* —microphotograms of the absorption spectra of two different thin Cu_2O films

Fig. 3. *a* —reflection spectrum of a wedge-shaped Cu_2O single crystal at $T = 4.2°K$; *b* —diagram of the splitting of spectrum 3a

carried out earlier in our laboratory on the influence of directed deformations of oriented Cu_2O crystals (^{6}) for the case when the second-order axis C_2 coincides with the direction of the incident light, and the axis of the applied stress is parallel to the fourth-order axis C_4. Although our observations of the polarization of the reflection lines refer only to one random crystal, they also testify in favor of the fact that the pattern observed in absorption, which is more complex in comparison with reflection, is caused by deformations.

Discussion and some conclusions. First of all it should be noted that the absorption coefficient in the blue and deep-blue regions of the spectrum is large, and the lines $\lambda_1^{(\mathrm{g})}$ and $\lambda_1^{(\mathrm{c})}$ are considerably more intense than, respectively, the

Figure 3

Figure 3: Figure 3

lines $\lambda_2^{(g)}$ and $\lambda_2^{(c)}$. On the basis of this fact, and also of Elliott' s theory (^{7}), we assume that the exciton lines in the blue and deep-blue regions are allowed and should be regarded as the first members $n = 1$ and $n = 2$ of hydrogen-like exciton series (Fig. 4)*.

$$\text{Blue series} \quad \nu_n^{(g)} = 21220 - \frac{368}{n^2} \text{ cm}^{-1}, \qquad n = 1, 2, ...$$

$$\text{Deep-blue series} \quad \nu_n^{(c)} = 22302 - \frac{415}{n^2} \text{ cm}^{-1}, \qquad n = 1, 2, ...$$

This assertion and the correctness of the band-structure scheme of Cu_2O given in Fig. 4 are confirmed by a number of experimental facts:

1. The differences of the boundary energies of the yellow and green series, on the one hand, and of the blue and deep-blue series, on the other, are equal.
2. The lines of the deep-blue series are appreciably broader than the lines of the blue series, just as the lines of the green series are noticeably broader than the lines of the yellow series. Both of these considerations were already cited in (^{1}).
3. The differences between the temperature coefficients of the yellow and green series in the interval 4.2—77.3°K, on the one hand, and of the blue and deep-blue series, on the other, are equal. From this experimental fact, namely that the temperature coefficient of the blue and deep-blue series is zero, it follows that the temperature coefficient for the subbands Γ_7^+, Γ_8^+, and Γ_{12}^- must also be equal to zero. Hence it follows that the nonzero temperature coefficient of the yellow and green series, $(1.1—1.2) \cdot 10^{-4}$ eV/deg, is determined by the temperature coefficient of the subband Γ_6^+, in agreement with the band scheme of Fig. 4.
4. If the band scheme of Cu_2O (Fig. 4) is correct, the following relation must hold between the Rydberg constants for the yellow, green, blue, and deep-blue hydrogen-like series:

$$\frac{R^{(c)} - R^{(g)}}{R^{(z)} - R^{(zh)}} = \frac{R^{(c)} R^{(g)}}{R^{(z)} R^{(zh)}} \tag{1}$$

provided that the dielectric constants $\varepsilon^{(zh)}$, $\varepsilon^{(z)}$, $\varepsilon^{(g)}$, $\varepsilon^{(c)}$ of the yellow, green, blue, and deep-blue exciton series are approximately equal.

This relation is in fact approximately satisfied if the experimental values for R are substituted: $R^{(zh)} = 780.7$, $R^{(z)} = 1200$, $R^{(g)} = 368$, $R^{(c)} = 415$ cm^{-1}. This fact shows that the first two lines of both the blue and the deep-blue exciton series, at least approximately, fit hydrogen-like series with the first quantum numbers $n = 1$ and $n = 2$, i.e., these lines belong to allowed direct transitions,

Fig. 4. Band scheme of Cu_2O according to the data of Refs. (6, 8-10)

Figure 4: Fig. 4. Band scheme of Cu_2O according to the data of Refs. (6, 8-10)

and not to forbidden ones. Indeed, if for the lines of the blue and deep-blue series one assumes a hydrogen-like dependence with the first quantum numbers $n = 2$ and $n = 3$, then for R the values obtained are: $R^{(r)} = 1987$ and $R^{(c)} = 2239$ cm^{-1}, and then relation (1) is not satisfied.

It is noteworthy that the Rydberg constants for the blue and violet series are appreciably smaller than for the yellow and green series. This shows that the effective mass of the electrons at the conduction subband Γ_{12}^- at $\vec{K} = 0$ is smaller than at the adjacent conduction subband Γ_6^+ at $\vec{K} = 0$, which is associated with the yellow and green series. It should also be noted that the splitting $\lambda_2^{(r)}$ is smaller than the splitting $\lambda_1^{(r)}$ (Fig. 2a). This phenomenon may be explained by a change in the effective mass of the electrons in each of the new subbands arising under deformation from the subband Γ_{12}^-, the effective mass of the upper of the new subbands decreasing in comparison with the effective mass of the undeformed subband Γ_{12}^-, while the effective mass of the lower one increases.

Fig. 4. Band scheme of Cu_2O according to the data of Refs. $^{6,8-10}$

The excitonic origin of the blue and violet lines of the Cu_2O crystal is also supported by the features of their position in the spectrum: each of these groups of lines adjoins a new edge of intense continuous absorption, which directly indicates the existence of a new band and of new exciton levels on its long-wavelength side.

It is interesting to compare the effect of stress for the blue and violet exciton series in absorption, on the one hand, and for the yellow and green exciton series, on the other hand. A similar and very strong effect of deformation is observed on the lines of the blue and violet series, causing their splitting in

---

* In the previous work (^{1}) we groundlessly assumed that the lines of the blue and deep-blue series correspond to the terms $n = 2$ and $n = 3$ of hydrogen-like exciton series corresponding to forbidden transitions. In addition, the band scheme of Cu_2O ((^{1}), Fig. 3) included a mistake, corrected in (^{1}) and in the scheme (Fig. 4) of the present work. Moreover, on the basis of studies of the influence of directed deformations on the lines of the blue and deep-blue series (^{6}), the upper conduction band should be assigned the symmetry not Γ_7^+, but Γ_{12}^-. Here we also give more accurate data for the wavelengths of the blue and deep-blue reflection lines: $\lambda_1^{(g)} = 4797$ Å, $\lambda_2^{(g)} = 4733$ Å, $\lambda_1^{(c)} = 4569$ Å, and $\lambda_2^{(c)} = 4505$ Å.

the spectrum. The effect of stresses on the exciton lines of the yellow and green series is also similar, but they are characterized by a small influence of stress and the absence of splitting [7]. These facts are an additional argument in favor of the view that the formation of excitons of the blue and violet series corresponds to the transition of electrons from the valence subbands Γ_7^+ and Γ_8^+ to the corresponding exciton levels near the higher-lying conduction subband Γ_{12}^-. Further, it may be concluded that for all four exciton series the effect of stresses is exerted mainly on the conduction band; under the action of stress the conduction subband Γ_6^+ is shifted slightly, while the conduction subband Γ_{12}^- is split into two subbands.

Received
18 VI 1962

REFERENCES

1. E. F. Gross, Chzhan Guan-in, *Fiz. tverd. tela*, **4**, 261, 827 (1962).
2. J. B. Grun, M. Sieskind, S. Nikitine, *J. Phys. Chem. Solids*, **21**, 119 (1961).
3. I. S. Gorban' , V. B. Timofeev, *Fiz. tverd. tela*, **2**, 1111 (1960).
4. M. Hayashi, *J. Phys. Soc. Japan*, **14**, 681 (1959).
5. I. Pastrnyak, *Fiz. tverd. tela*, **3**, 869 (1961).
6. E. F. Gross, V. T. Agekyan, A. A. Kaplyanskii, *Fiz. tverd. tela* (1962) (in press).
7. E. F. Gross, A. A. Kaplyanskii, V. T. Agekyan, *Fiz. tverd. tela*, **4**, 1009 (1962).
8. A. G. Zhilich, *Vestn. Leningr. univ.*, No. 22, 5 (1959); No. 10, 5 (1960).
9. S. A. Moskalenko, *Fiz. tverd. tela*, **2**, 1755 (1960); *Optika i spektroskopiya*, **9**, 369 (1960).
10. R. J. Elliott, *Phys. Rev.*, **108**, 1384 (1957); **124**, 340 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.