PHYSICS

Corresponding Member of the Academy of Sciences of the USSR E. F. GROSS and A. A. KAPLYANSKII

1960

SovietRxiv

Abstract

Full Text

PHYSICS

Corresponding Member of the Academy of Sciences of the USSR E. F. GROSS and A. A. KAPLYANSKII

OPTICAL ANISOTROPY OF CUBIC CRYSTALS CAUSED BY THE PHENOMENON OF SPATIAL DISPERSION. QUADRUPOLE EXCITON ABSORPTION OF LIGHT IN CUPROUS OXIDE

At the long-wavelength edge of the fundamental absorption of Cu_2O there is observed a complex structure in the form of two hydrogen-like series of absorption lines associated with the excitation of Mott excitons in the Cu_2O lattice (see the review (^{1})). On the long-wavelength side of the "yellow" series, which obeys the formula $\nu_n = (17460—785/n^2)$ cm^{-1} for lines with number $n \geq 2$, there is observed a line λ6125 Å, considerably weaker and narrower in comparison with the remaining members of this series, to which the number $n = 1$ is conventionally assigned. According to the existing interpretation, this line corresponds to excitation of the lowest, ground state of the excitons ($n = 1$); moreover, the considerable deviation of its position from that required by the Rydberg series formula is explained by the small radius of the excitons in this state, as a result of which the Wannier-Mott hydrogen-like model is unsuitable for calculating the energy of the state.

In investigating the absorption spectra of Cu_2O on single-crystal specimens ($T = 77$°K), we discovered a phenomenon unusual for cubic crystals: anisotropic absorption of light in the line with $n = 1$ (λ6125 Å)* (^{4}). It turned out that in the spectrum of light transmitted through a Cu_2O plate, the intensity of the λ6125 Å absorption line in two arbitrary mutually perpendicular states of polarization is, in general, not the same. The degree of polarization of the line, as well as its integrated intensity, varied strongly for different specimens, and also for one crystal when the direction of passage of light through the plate was changed. It was natural to suppose that these changes are connected with the different orientation of the crystallographic axes in different specimens.

It was of interest to determine the dependence of the intensity and polarization of the λ6125 Å line on the direction of propagation of light in the crystal lattice of the specimen. For this purpose, a sufficiently large single crystal of Cu_2O was grown. Then, from Laue X-ray photographs obtained by the method, the orientation of the crystallographic axes in the specimen was determined, and plates

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

differently oriented with respect to the crystallographic axes were then cut from it. In particular, plates of equal thickness were cut with planes perpendicular to crystallographic symmetry axes of the 4th (C_4), 3rd (C_3), and 2nd (C_2) orders. The absorption of light in the $\lambda 6125$ Å line was studied in such plates cut from a single crystal, as well as in separate independent single-crystal specimens with an orientation of the axes determined from Laue photographs.**

* The anisotropy of light absorption in the line persisted both when the specimens were cooled to $T = 4.2$°K and when they were heated to temperatures close to 0°C (until the line became unobservable because of thermal broadening).

** The authors are grateful to M. A. Rumsh and V. N. Shchemelev for the X-ray determination of the orientations in some of the Cu_2O specimens studied by us.

Fig. 1. Spectrograms of the absorption line $n = 1$ ($\lambda\,6125$ Å) of the yellow exciton series in Cu_2O for the passage of polarized light in the direction L through single-crystal plates cut along different crystallographic planes (hatched), perpendicular to the 4th-, 3rd-, and 2nd-order symmetry axes (C_4, C_3, and C_2). $\lambda_1 = 6164$ Å and $\lambda_2 = 6086$ Å are the long-wavelength edges of the continuous-absorption steps.

These investigations established that the intensity and degree of polarization of the line $\lambda 6125$ Å are completely determined by the orientation of the light beam L (i.e., the direction of observation) relative to the axes of the crystal lattice of the specimen (Fig. 1). Under normal incidence of light on a plate whose plane coincides with the plane of the crystallographic cube ($L \parallel C_4$), the absorption line is relatively intense and unpolarized (Fig. 1, *a*). Under normal incidence of light on a plate whose plane is the plane of the crystallographic octahedron ($L \parallel C_3$), the line is also unpolarized, but its intensity is considerably lower than for $L \parallel C_4$ (Fig. 1, *b*). Under normal incidence of light on a plate whose plane corresponds to the crystallographic plane of the rhombododecahedron ($L \parallel C_2$), the line is intense and completely polarized with the electric vector $\mathbf{E}$ perpendicular to the plane of the cube in which the axis C_2, which is the direction of observation, lies (Fig. 1, *c*). The described character of absorption in the line occurs correspondingly when observing along all symmetry axes of the crystal of fourth ($3C_4$), third ($4C_3$), and second ($6C_2$) order.

Fig. 2. Diagram of the intensity and polarization state of the absorption line $n = 1$ ($\lambda 6125$ Å) as a function of the direction of light propagation in the Cu_2O crystal lattice

In the general case, when L does not coincide with the symmetry axes of the crystal, the line $\lambda 6125$ Å is partially polarized. The change in the intensity and polarization of the line for the most characteristic cases of a gradual transition of the observation direction from one symmetry axis to another is shown schematically in Fig. 2. The coordinate system here is combined with the triad of cube axes ($3C_4$), and the direction of the beam L is determined by the angles ϑ and φ. We shall consider the intensity of the line in two mutually perpendicular polarization states, corresponding to oscillations of the electric vector $\mathbf{E}$ in the meridional plane containing L, I_ϑ, and normal to it, I_φ. The lengths of the arrows in Fig. 2 are related to the quantities I_ϑ and I_φ, showing the corresponding direction of oscillations of $\mathbf{E}$.

When the direction of observation changes from the position $L \parallel C_4$ ($\parallel Ox$) to $L \parallel C_2$ ($\parallel Ou$) in such a way that it remains in the plane of the cube xOy, while the angle φ gradually increases from 0° (where $L \parallel C_4$ and $I_\vartheta = I_\varphi$), the intensity I_ϑ does not change, whereas I_φ decreases monotonically. At $\varphi = \pi/4$, corresponding to the direction of the beam along C_2, I_φ becomes equal to zero, i.e., the line proves to be completely polarized. With a further increase of the angle φ, the intensity I_φ again becomes noticeable and increases, becoming equal, at $\varphi = \pi/2$ ($L \parallel Oy \parallel C_4$), to the unchanged I_ϑ. Let now the direction of observation change from the position $L \parallel C_2$ ($\parallel Ou$) to $L \parallel C_4$ ($\parallel Oz$) in such a way that L remains in the plane of the rhombododecahedron zOu. At $\vartheta = \pi/2$ ($L \parallel C_2$) the line is completely polarized ($I_\varphi = 0$). As ϑ decreases, the appearance and strengthening of I_φ are observed and, conversely, a significant weakening of I_ϑ. At ϑ close to $\arccos \frac{1}{\sqrt{3}}$, corresponding to the direction of observation along C_3, the intensities become equal, $I_\vartheta = I_\varphi$. With a further decrease of ϑ, the intensity I_φ becomes greater than I_ϑ. As ϑ approaches 0°, the intensities increase in both polarization components, and for $L \parallel Oz \parallel C_4$ the intensities again become equal, $I_\vartheta = I_\varphi$. The described behavior of the line for the most characteristic

upon changes in the direction of observation within a single octant, has a completely analogous form for all other octants. Thus, the spatial distribution of the intensity and polarization state of the line possesses the symmetry elements of the cube and, with respect to absorption in the $\lambda 6125$ Å line, the Cu_2O crystal has—if only the polarization, but not the absorption intensity, is taken into account—7 "optical axes" ($3C_4$ and $4C_3$), along which the absorption is isotropic.

The observed optical anisotropy of absorption of the cubic Cu_2O crystal cannot be explained within the framework of ordinary crystal optics, in which cubic crystals are optically isotropic. Nor does it seem possible to interpret the phenomenon as the result of some "noncubicity" of the Cu_2O lattice, or to assign it to the class of phenomena observed in cubic crystals containing local anisotropic centers*. First of all, the fact that the spatial distribution of the intensity and polarization of the absorption in the line possesses the symmetry elements of the cubic crystal argues against these assumptions.

The anisotropy of the λ6125 Å absorption line of the cubic Cu_2O crystal can, in our opinion, be explained by the fact that the optical transition corresponding to the line is not an ordinary dipole transition, but a transition of higher multipolarity—an electric quadrupole transition. Indeed, the observed dependence of the intensity and polarization of the line on the direction of the ray in the lattice corresponds to the spatial distribution of the field of an electric quadrupole system, which is equivalent to three elementary plane quadrupoles arranged in the lattice normal to the three C_4 axes, or to four linear quadrupoles oriented along the four C_3 axes. According to ($^{6-8}$), the emission (absorption) of such a quadrupole system in the directions of the coordinate axes of the cube ($3C_4$) should be unpolarized; in the directions of the face diagonals of the cube ($6C_2$), completely polarized with **E** parallel to the cube axis perpendicular to the diagonal; and in the directions of the body diagonals of the cube ($4C_3$), unpolarized, with an intensity three times smaller than for $L \parallel C_4$. This is precisely the character of the experimental dependence for the λ6125 Å line in the Cu_2O spectrum, which directly indicates that the absorption in the λ6125 Å line is purely quadrupole**.

As far as we know, quadrupole optical transitions in a solid (as, in general, in the condensed phase) have never previously been observed experimentally; nor has the optical anisotropy of cubic crystals associated with such transitions been observed. As for the theoretical consideration of the question, it is interesting to note that already in the work of H. A. Lorentz on the electronic theory of the dispersion of crystals, in a higher approximation of the theory it was found that cubic crystals possess birefringence(^{11}). In this case the birefringence is maximal when light propagates along $6C_2$ and is absent when light propagates along the axes $3C_4$ and $4C_3$ (i.e., cubic crystals are optically semiaxial!). According to Hellwege(^{9}), the physical meaning of this higher approximation, which gives anisotropy, consists in taking into account the contribution to the dispersion of the crystal, in addition to the ordinary dipole interaction of light with matter,

---

* This fact consists in the appearance of absorption dichroism in the spectra of centers as a result of anisotropic photochemical transformations of the centers under the action of polarized light(^{5}).

** The assumption of a quadrupole explains the observed characteristic phenomenon, which is difficult to understand for dipole absorption of light. It consists in the fact that, when a Cu_2O crystal is rotated about the vertical axis and observation is made in the horizontal direction, changes in the intensity of the λ6125 Å line occur in the absorption spectrum in both polarization components with oscillations of **E** in the horizontal and vertical planes. This is especially noticeable when L, varying in the horizontally situated plane of the rhombic dodecahedron, passes through the direction C_3.

also of quadrupole interaction. In (9) it was shown that quadrupole transitions can also lead to anisotropic emission and absorption of light by cubic crystals.

Thus our experimental results confirm Hellewege' s prediction concerning the possibility of anisotropy of optical absorption in cubic crystals due to quadrupole transitions. Recently, the possibility of optical anisotropy in cubic crystals was theoretically shown in studies by Pekar (12) and Pekar et al. (13) on the propagation of light in crystals in which excitons arise, and in the work of Ginzburg (14), where the spatial dispersion of light was taken into account.

The established quadrupole character of the absorption of light in the line $\lambda 6125$ Å is consistent with the observed low intensity of the line and testifies in favor of the exciton interpretation of the line. Indeed, the usually observed coefficient of allowed dipole absorption of light in the fundamental lattice of crystals has the value $k \approx 10^6$ cm^{-1}, which gives for the coefficient of quadrupole absorption in the fundamental lattice (its intensity is related to the dipole one as $(2\pi a/\lambda)^2 \simeq 10^{-6}$, where a is a length of the order of atomic size) a value consistent with that estimated experimentally ($k \simeq 10$ cm^{-1}) (10) for the line $n = 1$. The quadrupole character of the line can also explain the observed absence of remission from the ground state of excitons in Cu_2O, since, with the low probability of an optical quadrupole transition (lifetime $\simeq 0.1$ sec), the excited state will always be destroyed in some competing annihilation process.

It should be noted that anisotropic absorption was observed by us only for the line $\lambda 6125$ Å. A study of light absorption in other elements of the structure of the absorption edge of Cu_2O—in the steps, in the lines of the yellow exciton series with $n \geq 2$, and also in the so-called "new" lines located between the members of the yellow series and observed at $T = 4.2°$ K—showed that it is isotropic. This points to the distinctiveness of the ground state of the exciton in Cu_2O as compared with the excited exciton states.

The experimental detection of a quadrupole transition in the line $n = 1$ of the exciton spectrum in Cu_2O imposes substantial additional requirements on the theory of the ground exciton state of the crystal. In this theory, dipole transitions to the ground exciton state must be forbidden and quadrupole transitions allowed. It is interesting to note in this connection that the quadrupole character of the line agrees with Elliott' s conclusions (3) concerning the forbiddenness of dipole transitions to the ground state of the exciton in Cu_2O; however, the hydrogen-like model used in (3) is hardly suitable for an exciton of small radius with $n = 1$. At the same time, Zhilich' s model (2), which gives a value of the excitation energy of the ground exciton state consistent with experiment, leads to the allowance of dipole transitions to this state.

Physical-Technical Institute
Academy of Sciences of the USSR

Received
2 February 1960

REFERENCES

1. E. F. Gross, *Usp. fiz. nauk*, **63**, 575 (1957); *Nuovo Cim. Suppl.*, **4**, 672 (1957).
2. A. G. Zhilich, *Vestn. LGU*, No. 4 (1957).
3. R. S. Elliott, *Phys. Rev.*, **108**, 1384 (1957).
4. E. F. Gross, A. A. Kaplyanskii, *Fiz. tverd. tela*, **2**, No. 2 (1960).
5. P. P. Feofilov, *Usp. fiz. nauk*, **58**, 69 (1956).
6. A. Rubinowicz, J. Blaton, *Ergebn. d. Exakt. Naturwiss.*, **11**, 176 (1932).
7. M. A. Elyashevich, *Spectra of Rare Earths*, 1953.
8. D. Stratton, *Theory of Electromagnetism*, 1948.
9. K. H. Hellewege, *Zs. f. Phys.*, **129**, 626 (1951).
10. I. Pastrnyak, Candidate' s dissertation, Physico-Technical Institute, Academy of Sciences of the USSR, 1959.
11. H. A. Lorentz, *Verh. d. k. Akad. v. Wet. Amsterdam*, **18** (1879).
12. S. I. Pekar, *ZhETF*, **33**, 1022 (1957); **34**, 1176 (1958); **36**, 451 (1959).
13. S. I. Pekar, B. E. Tsekvava, *Fiz. tverd. tela*, **2**, 261, 482 (1960).
14. V. L. Ginzburg, *ZhETF*, **34**, 1593 (1958).

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

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