



Title	Absorption Spectrum of Cuprous Oxide in the Visible Region
Author(s)	Hayashi, Masakazu
Citation	北海道大學理學部紀要, 4(2), 107-128
Issue Date	1952-03
Doc URL	http://hdl.handle.net/2115/34194
Type	bulletin (article)
File Information	4_P107-128.pdf



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Absorption Spectrum of Cuprous Oxide in the Visible Region

Masakazu HAYASHI

(Received September 1, 1951)

The absorption coefficient of cuprous oxide crystal is very large in the region of shorter wave-lengths than 600 $m\mu$. However, owing to the success in preparing a very thin plate of cuprous oxide and in constructing special absorption tubes, we could take its absorption spectrograms by the use of Hilger's E_1 type spectrograph, whose maximum dispersion was 40 $\text{\AA}/\text{mm}$ in the region in question. There appeared i) two sharp absorption edges forming a doublet, ii) hydrogen-like absorption lines adjoining an absorption band, and iii) another absorption band at the wave-length much shorter than those of the hydrogen-like lines. The doublet separation is found to be 0.023 eV (226 cm^{-1}), which coincides with that of the ground state 2P of O^- . Thus, we arrive at the conclusion that the filled band of cuprous oxide corresponds to $(2p)^6$ of O^{--} . The energies of the two absorption edges are 2.032 eV and 2.004 eV at 0°K and coincide, within the estimated error, with that of electron affinity of oxygen atom. These edges are, therefore, interpreted as the so-called electron affinity spectrum in absorption. As regards the hydrogen-like lines, they can be expressed by the equation $E(\text{eV}) = 2.161 - 0.090/n^2$ (at -184°C), of which the absorption line corresponding to $n = 1$ is missing, and their series limit corresponds to the energy of the lowest level of the empty band. Further, the temperature dependency of the two absorption edges and the hydrogen-like lines has been investigated in the region between -184°C and $+150^\circ\text{C}$. The obtained results are in qualitative agreement with the theoretical expectation. The other absorption band mentioned above seems to indicate the splitting of the empty band and to support the opinion for some crystals (Cu_2O , etc.) of BRUNING and DE BOER, who studied the secondary electron emission of ionic crystals.

§ 1. Introduction.

The phenomena, in which the electrons in a crystal are concerned, i. e. optical, electric, and magnetic properties of a crystal, will not be explained in a satisfactory way, unless the electronic structure of the crystal is fully investigated. The study of absorption spectrum provides a powerful means for the investigation, since the absorption of photo-quantum gives rise to an electronic transition from any level first occupied by the electron to the level

permitted by the selection rule and the absorbed quantum energy can be determined by observing the absorption spectrum. The best known examples are a series of researches on the absorption spectra of alkali-halides, which have been carried out by Göttingen School and others. Besides the alkali-halides, the crystals such as Ag-, Pb-, Tl-, Cd-, Zn-, Ni-, and Co-halides¹⁾ and Cu_2O ²⁾ have been subjected to the investigation of their absorption spectra, but thus far only poor results have been obtained, mainly because their strong characteristic absorption, in which every atom of the crystal participates, extends into the visible region.

FIGAREW and GOLOUB³⁾ measured the absorption coefficient of cuprous oxide. Their results, published in a short note, may be quoted as follows: The absorption coefficient is 3,200 per cm at wave-length $500 \text{ m}\mu$ and as the wave-length increases from $500 \text{ m}\mu$ to $600 \text{ m}\mu$ it decreases linearly down to 250 per cm at $600 \text{ m}\mu$. In the region between $600 \text{ m}\mu$ and $740 \text{ m}\mu$ it continues to diminish slowly with the wave-length until it practically vanishes at $740 \text{ m}\mu$. The rate of decrease seems to change suddenly at $600 \text{ m}\mu$, probably corresponding to the wave-length of an absorption edge.

Owing to the very large absorption coefficient of cuprous oxide, we have an immense deal of trouble in the investigation of its spectrum. This is the reason why most of the hitherto pursued methods have been confined to the investigation of phenomena accompanying the absorption of photo-quanta, such as the inner or outer photo-electric effect, the photo-electromotive force, and so forth.

SCHÖNWALD³⁾ studied the inner photo-electric effect of cuprous oxide and found three peaks of the so-called primary photo-current, their wave-lengths being 2.0μ , 0.8μ , and 0.63μ . The intensity of the peak at 0.8μ varies, depending on the samples; in some of them it disappears completely. Since the wave-length corresponding to the peak of the primary photo-current should coincide with that of the absorption edge, it follows that there are three absorption edges at wave-lengths 2.0μ (0.6 eV), 0.8μ (1.5 eV), and 0.63μ (2.0 eV), the edge at 0.63μ corresponding to that observed at $600 \text{ m}\mu$ by FIGAREW and GOLOUB described above. For the energies of the absorption edges discovered by SCHÖNWALD, MOTT and GURNEY⁴⁾ gave the following interpretation: 2.0 eV corresponds to the energy difference between the filled and the empty band, and 0.6 eV to that

between the filled band and an impurity level, the difference between this level and the empty band being 1.5 eV.

The present writer succeeded in taking photograph of the absorption spectrum of cuprous oxide by using a spectrograph with large dispersion and found that the absorption edge corresponding to that at 0.63μ observed by SCHÖNWALD in his research of primary photo-current has a certain definite structure. Moreover, the writer found new absorption bands in the spectrum taken at low temperatures (down to liquid air temperature), and also, by studying the temperature dependency of the absorption edges, reached the conclusion that the dependency coincides in the main with the tendency expected theoretically.

§ 2. Preparation of Sample.

Since the absorption coefficient is very large as stated in § 1, it is necessary to make the sample, whose absorption spectrum is to be investigated, as thin as possible. The copper plate used for preparing the sample was from 0.02 mm to 0.1 mm thick, and 5 mm \times 20 mm or 3 mm \times 10 mm in size.

The reversible reaction between cuprous and cupric oxides and that between cuprous oxide and copper are represented by the equations: $2\text{Cu}_2\text{O} + \text{O}_2 \rightleftharpoons 4\text{CuO}$ and $2\text{Cu}_2\text{O} \rightleftharpoons 4\text{Cu} + \text{O}_2$, respectively. The relation between pressure and temperature at equilibrium for both of these reactions was determined by IIDA.⁵⁾ According to his results, the equilibrium pressure of oxygen gas in the former reaction is, for instance, 95.3 mm Hg at 1,000°C, and in the latter 0.028 mm Hg at 1,115°C. The cuprous oxide is, therefore, to be obtained, if copper is oxidized at suitable pressure and temperature. After many trials, the writer prepared the sample at the selected temperature 950°C and pressure 20 mm Hg of oxygen gas.

Figure 1 shows the apparatus used for oxidizing the sheet of copper. An alumina boat containing two or three sheets of copper is put in a quartz-tube, which is set in an electric furnace, so that the boat may be located at the center of the furnace. Oxygen gas produced by means of electrolysis of water passes through a drying column containing P_2O_5 -powder and then is stored in a reservoir. Lest the pressure of the oxygen gas filled in the quartz-tube should exceed that indicated above, the gas in the reservoir

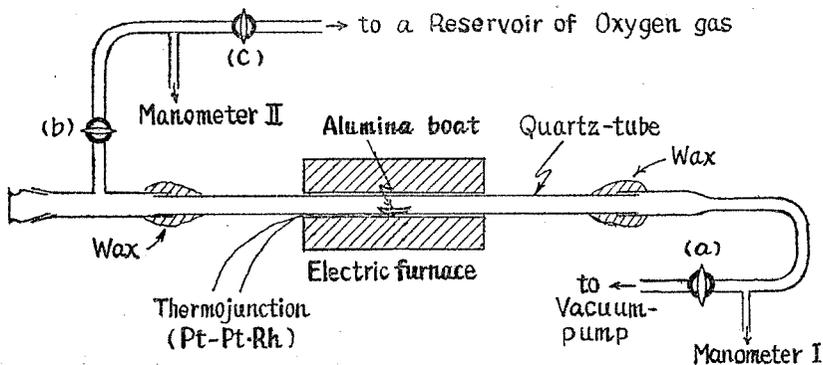


Fig. 1. Apparatus used for preparing the sample.

is made to expand by two steps. First it is let into a chamber provided with a manometer II, whose volume is about one-fifth that intercepted by stop-cocks (a) and (b) including the quartz-tube. The pressure of the gas to be introduced into the quartz-tube can therefore be estimated beforehand by making use of the manometer II. The desired pressure in the quartz-tube can be secured by observing the manometer I, while the gas is slowly introduced through the stop-cock (b).

The procedure of preparing the sample is as follows. The quartz-tube is evacuated through the stop-cock (a) by means of a high speed vacuum-pump and then heated by closing the circuit of the electric furnace until its temperature rises up to 950°C . Next the stop-cock (a) is closed and the oxygen gas is let into the quartz-tube until the manometer I indicates the pressure 20 mm Hg. The pressure decreases as long as the oxidation continues, so that the oxygen gas must be supplemented occasionally. Under these conditions it takes about 30 minutes for the oxidation to be completed. The sample is left in the furnace for further 20 or 30 minutes, and finally, by opening the electric circuit, the furnace is cooled down and at the same time the pressure of the gas is made to decrease gradually, so that the chamber may be completely evacuated when the temperature is down to 900°C . In this way, the cuprous oxide sample with fairly good transparency for red light is obtained. It is, however, very *brittle*. Experience shows that the better and more transparent sample can be prepared, if, after completion of oxidation at 950°C , the pressure of gas is

reduced to 5 mm Hg at the same constant temperature and it is left intact for more than two hours, without any further change of condition.

§ 3. Experiment.

The spectrograph mainly made use of was of Hilger E₁ type, whose maximum dispersion in the region in question was 40 Å/mm. Hilger's constant deviation spectrograph, whose dispersion in the same region was 150 Å/mm, was also used as an auxiliary. The dry plate used was the hypersensitive panchromatic plate supplied from Oriental Photo-Industrial Co. As light source served an incandescent lamp of 400 Watt.

(i) Absorption spectrum at room temperature.

Figure 2 is the reproduction of the absorption spectrograms taken at room temperature for thin plates of cuprous oxide, (a) and (b) corresponding to the samples 0.1 mm and 0.05 mm thick respectively. As will be seen from Fig. 2 (a), there appear two sharp absorption edges at $0.628_2 \mu$ and $0.637_3 \mu$, which will be denoted by "the absorption edges (a)" or simply by "(a)" hereafter. The spectrum (Fig. 2 (b)) shows another absorption edge at 0.591μ to be denoted by "the absorption edge (b)" or simply by "(b)," and, besides, on its longer wave-length side at least two absorption bands at 0.597μ and 0.593μ , whose breadth is relatively narrow. As will be stated in the next subsection (ii), the breadth of these bands becomes much narrower at low temperatures and they come out to be distinctly observed (see Fig. 8). The values of their wave-lengths here given are, therefore, not very accurate.

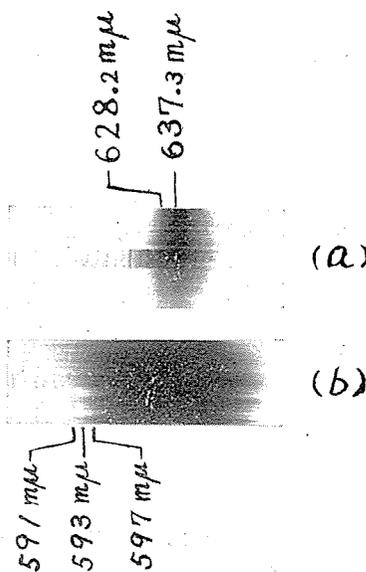


Fig. 2. Absorption spectrum of cuprous oxide taken at room temperature: (a) corresponds to the sample 0.1 mm thick and (b) to that 0.05 mm thick.

The absorption edges (a) correspond to that at 0.63μ discovered by SCHNÖWALD mentioned in §1. Thus, it is found that the absorption edge at 0.63μ due to SCHÖNWALD is not simple, but has a doublet structure.

The absorption edge (b) is not very sharp, but has "skirts" on its longer wave-length side, which increase in intensity with increasing thickness of the sample. For the sample of 0.1 mm thickness, for example, the "skirts" extend up to 0.606μ as estimated on the spectrogram,⁶⁾ and mask the above-mentioned absorption bands altogether. The meaning of this phenomena will be discussed later in §4.

(ii) Temperature dependency of absorption edges and bands.

The temperature dependency of the absorption edges and bands mentioned in subsection (i) was investigated in the two separate regions of temperature.

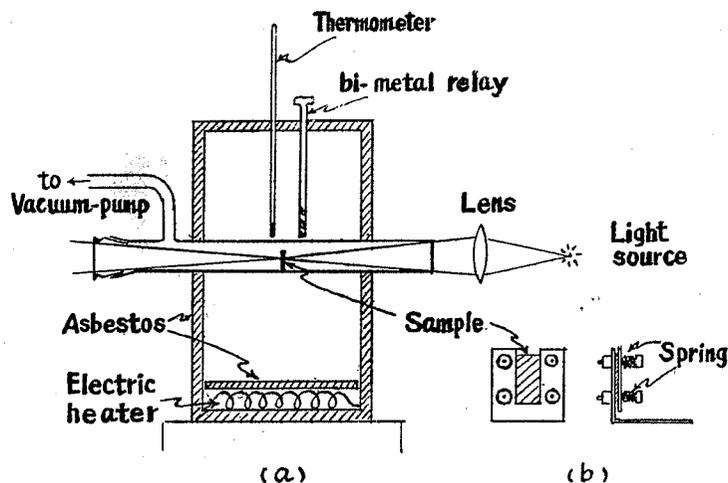


Fig. 3. (a) Absorption tube used in the region of higher temperatures above 0°C and the thermostat.
(b) Sample-holder made of bronze.

In the region of higher temperatures above 0°C the absorption tube shown in Fig. 3(a) was used. The thermostat, in which the absorption tube is to be placed, has the capacity $17 \times 17 \times 30\text{cm}^3$ and is made of asbestos plates of 1 cm thickness. The temperature is controlled by an electric heater (500 Watt) set at the bottom of the thermostat, whose current is regulated by a slidac. By a

sheet of asbestos put on the heater the absorption tube among others is protected from the direct radiation from the heater. Finer regulation of temperature was attained by the use of a bi-metal relay, and each desired temperature could be kept constant within the error $\pm 0.5^\circ\text{C}$. The temperature was measured by means of both a mercury thermometer fixed near the absorption tube and a thermojunction, whose elements are constantan and copper, inserted in the absorption tube. The absorption tube, made of hard glass, is connected to a vacuum-pump. The sample is held between two bronze frames, as shown in Fig. 3(b). As the thin plate of cuprous oxide is too brittle to stand strong pressure, it is just held in position by means of weak springs.

Thus, the temperature dependency of the absorption edges and bands was studied in the region between 0°C and 150°C . The results obtained show clearly the fact that the absorption edges (a) and (b) and the two narrow absorption bands lying in proximity to (b) are all shifted towards *red* as temperature rises. (The absorption edges (a) at 150°C lie in the wave-length region corresponding to the limit of sensitivity of the dry plate used, which is the reason why the study could not be extended to higher temperature region beyond 150°C .) Further important results obtained are:—

- (1) The energy difference (in eV) between the two absorption edges (a) remains constant (0.028eV), being independent of temperature ;
- (2) The shift of the absorption edges (a) is linear function of temperature, its gradient being $(3.8 \pm 0.2) \times 10^{-4}$ eV/deg ;
- (3) Similar relation holds both for the absorption edge (b) and the two absorption bands, with common gradient about 3×10^{-4} eV/deg ;
- (4) The energy difference between the two absorption bands is constant independent of temperature ;
- (5) As the temperature rises, the two absorption bands become more and more diffuse, such that only the one with longer wave-length can barely be observed at 40°C .

The results stated above are illustrated by the right-hand portion of the curves (a) and (b) in Fig. 5. Here (a) and (b) refer to the absorption edges (a) and (b) respectively. The dashed curves beneath the curve (b) indicate the temperature dependency of the

two absorption bands. When the thickness of the sample amounts to 0.1 mm, the absorption represented by the curve (*b*) extends as far as the curve (*b'*).

In the region of lower temperatures below 0°C the absorption tube (A) shown in Fig. 4 was used. The space between the double walls of a *Dewar*-vessel and that in the absorption tube are connected together and can be evacuated by a mercury diffusion pump through a three-ways stop-cock (*a*). The same sample-holder as shown in Fig. 3 (*b*) is laid at the center of the absorption tube. A thermojunction, consisting of constantan and copper elements, is introduced into the tube through the *Apiezon* wax "W" which serves as the cementing material of the windows of the tube (A).

After the absorption tube is highly evacuated, liquid air is let into the *Dewar*-vessel; then, the temperature of the sample falls down to about -10°C, which remains constant for a sufficiently long time to take a spectrogram. Now, if by turning the stop-cock (*c*) the dried air is introduced slowly into the absorption tube, the temperature of the sample begins to fall further down. The lowest temperature attainable in this method was -163°C.

The temperature dependency in the region of lower temperatures down to -163°C is shown by the left-hand portion of the curves (*a*) and (*b*) in Fig. 5. Here the curves assume the form entirely different in character from that in the region of higher temperatures, each of the curves tending to the respective critical point. The energy difference between the two absorption edges (*a*), however, remains the same as in the region of higher temperatures.

The two absorption bands near the edge (*b*) become increasingly sharper as temperature drops down, and, what is more, there appears a third band on the shorter wave-length side of the two bands and in immediate proximity to the edge (*b*). These absorption bands, three in all, undergo the same shift with variation of temperature as that of the edge (*b*), the energy differences among them always remaining constant. As regards these three bands, more details will be given in the next subsection (iii).

Addendum:—The constantan-copper thermojunction used in the study of the temperature dependency in the region of lower temperatures was calibrated, taking as standards the melting points of mercury (-39°C), chloroform (-63.5°C), and carbon disulphide (-112°C).

Fig. 4. Absorption tube (A) used in the region of lower temperatures below 0°C .

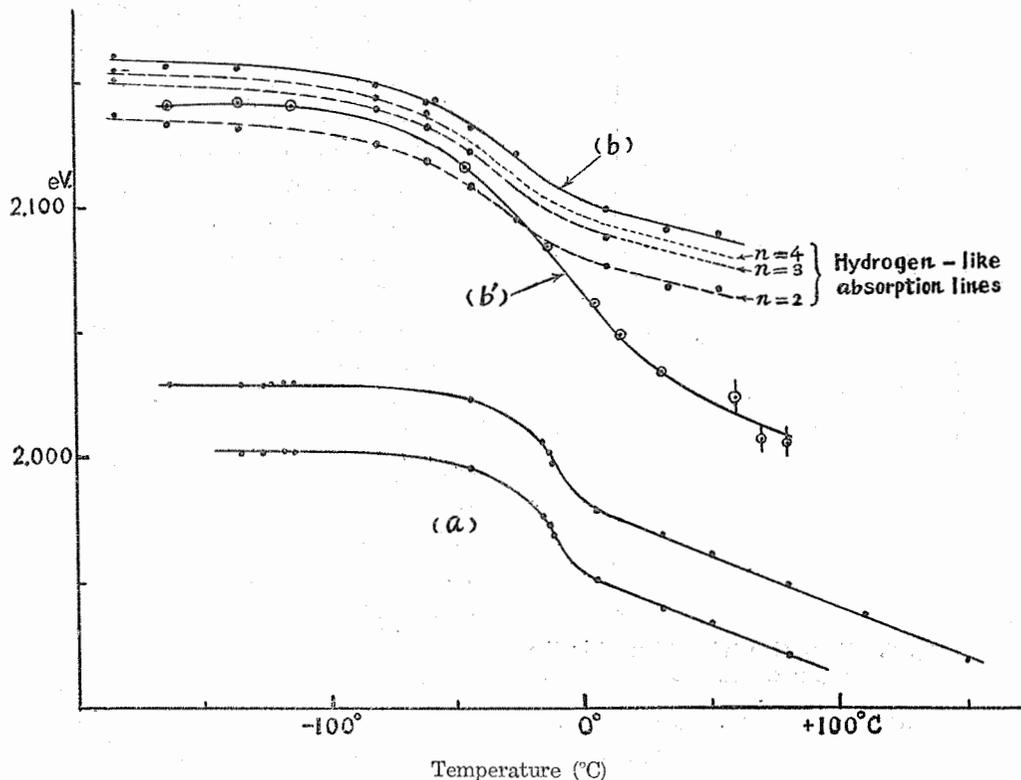
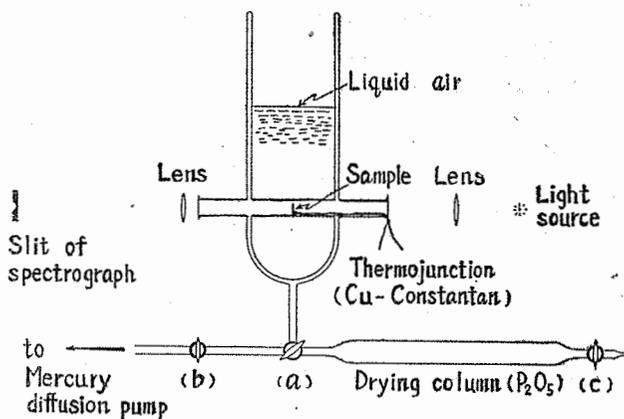


Fig. 5. Temperature dependency of the absorption edges and bands of cuprous oxide: The curves (a) and (b) indicate the temperature dependency of the edges, (a) and (b) respectively, and the dashed curves beneath the curve (b) that of the absorption bands near the edge (b); the curve (b') indicates the dependency of the absorption edge of the sample of 0.1 mm thickness corresponding to the edge (b).

(iii) Three narrow absorption bands.

The three narrow absorption bands mentioned above can be most distinctly observed by using the absorption tube (B) shown

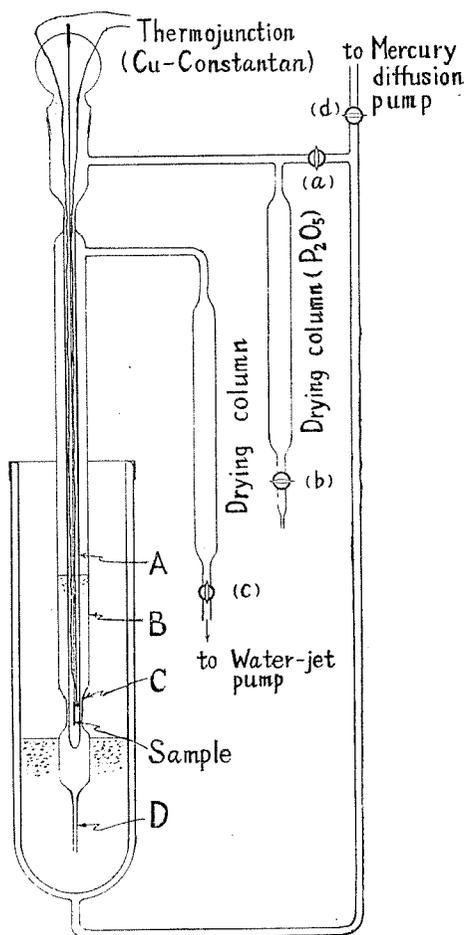


Fig. 6. Absorption tube (B) used in the region of lower temperatures.

in Fig. 6, instead of the tube (A) (Fig. 4), which is inconvenient for replacing the sample with another. The principal part of the absorption tube (B) consists of a double-walled tube, denoted by A and B in the figure. The sample is attached to the tip of a wire hung down from the top of the inner tube A. The outer tube B is connected with a water-jet pump through a side tube at the top and with a Dewar-vessel through a capillary tube D at the bottom, while both the tube A and the space between the double walls of the Dewar-vessel are evacuated by a mercury diffusion pump.

It is already known that the liquid air has strong absorption bands* in its spectrum, and that just in the region we are interested in. The thickness of the layer of liquid air, coming into the beam of light, must, therefore, be made

as thin as possible. Obviously, the surface of liquid air introduced into the Dewar-vessel must be kept constantly at the level below the beam of light. Now, by operating the water-jet pump, the liquid air is sucked up into the tube B up to the height beyond

* The wave-lengths at the maxima of absorption intensity are, according to the measurement by the writer, 631, 577, 532, and 477 m μ . These bands are interpreted as due to van der Waals' molecule (O₂)₂.⁷⁾

the part C, where the outer tube forms such a narrow neck, that it makes contact with the inner tube. The layer of the liquid air coming into the beam of light is thus made extremely thin. In fact, in the absorption spectrum no trace of absorption due to liquid air could be detected. Finally, if the dried air is gradually let into the tube A through the stop-cock (b), the temperature of the lower part of the tube A begins to fall rapidly, until it reaches -184°C , the lowest temperature attainable in this procedure.

Figure 7 shows another modified form of the absorption tube—which shall be designated by (C)—used in the study of the absorption spectrum in the region of low temperatures. Here it is intended to get rid of the fault that is inherent to the tube (B), that is, that there are too many glass-layers which intervene in the beam of light and cause the diminution of light intensity. The sample is cooled down by thermal conduction through a thick copper column, capped with a thick hollow cylinder also made of copper. The vessel, in which the cooling column is sealed, must be evacuated in order to avoid the convection effect. The tempera-

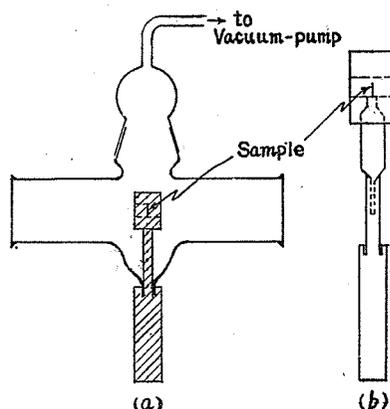


Fig. 7. Absorption tube (C) used in the region of lower temperatures.

ture attained by the use of this absorption tube was not so low as that obtained with the tube (B).

Figure 8 gives an example of the spectrograms taken by the use of tubes (B) and (C). The breadth of each of the three absorption bands is about 6\AA (0.002 eV) at -184°C and about 9\AA (0.004 eV) at -80°C . The wave-lengths and energies of these bands (referring to the center of each band) at two

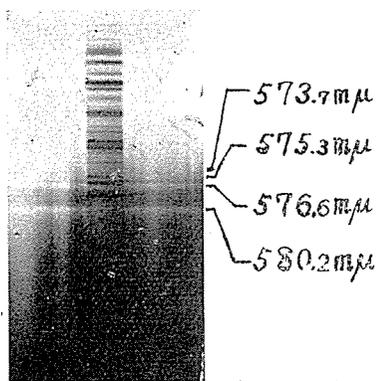


Fig. 8. Structure of absorption edge (b), ($\times 3$).

specified temperatures are given in TABLE I.

TABLE I. *Three absorption bands near the edge (b)*

- 80°C		- 184°C	
0.578 ₆ μ	2.142 eV (0.004)	0.575 ₃ μ	2.155 eV (0.004)
0.580 ₂	2.138 (0.013)	0.576 ₆	2.151 (0.014)
0.583 ₅	2.125	0.580 ₂	2.137

(iv) A new absorption band.

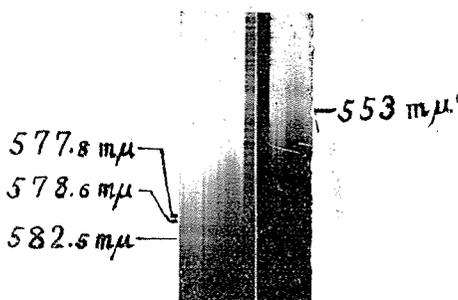


Fig. 9. A new absorption band appearing on the shorter wave-length side of the edge (b).

In the absorption spectrum taken at -130°C with the sample of 0.02 mm thickness, there appears a new absorption band at $0.553\ \mu$, that is on the shorter wave-length side of the absorption edge (b) (see Fig. 9). The interpretation for this, together with those for the absorption edges (a), (b), and the three absorption bands, will be given in §§4 and 5.

§ 4. Discussion of Temperature Dependency of Absorption Edges.

The temperature dependency of the energy bands in a crystal has been treated theoretically by PENNINGTON,⁸⁾ RADKOWSKY,⁹⁾ MUTO and ÔYAMA¹⁰⁾ among others.

PENNINGTON's theory is based upon the assumption that the effect of temperature on energy bands is only due to the temperature dependency of the lattice constant. He obtained the relation $d\nu/dt = -2\alpha\nu_0$, where ν and ν_0 are the frequencies of the absorption minimum at $t^{\circ}\text{C}$ and 0°C respectively and α the linear expansion coefficient of the crystal in question. For silber, whose absorption minimum appears at $324\ \text{m}\mu$ at room temperature, $d\nu/dt = -1.3 \times 10^{-4}\ \text{eV/deg}$, i. e. the frequency of the absorption minimum must

decrease linearly with increasing temperature, the result which conforms to the empirical fact.

For ionic crystals, however, the temperature dependency cannot be interpreted simply by considering the effect of thermal expansion of the crystal,¹¹⁾ since the interaction between electrons and lattice vibrations must be regarded as strong. Taking this into account, RADKOWSKY, MUTO and ÔYAMA discussed the case of ionic crystals. The interaction between electrons and lattice vibrations has two different effects; one is of *radiation damping* type and the other of *self-energy* type. The former effect was investigated by RADKOWSKY and the latter by MUTO and ÔYAMA. Generally speaking, the distribution of phonons at thermal equilibrium is subject to the Planck's law. But they treated the problem, dividing the temperature region into two extremes: $T \gg \theta$ and $T \ll \theta$, where θ is the characteristic temperature of the crystal. For $T \gg \theta$, MUTO and ÔYAMA obtained the formula

$$E = a - bT, \quad (1)$$

and, for $T \ll \theta$,

$$E = a' - b' \exp(-\theta/T), \quad (2)$$

where E is the energy of the absorption edge, and a , b , a' , b' the constants characteristic of the crystal in question.

The results obtained by the present writer are just in accordance with these theoretical results, since the right-hand branches of the curves (a) and (b) in Fig. 5 can be expressed by linear functions, and the left-hand branches by exponential functions. Thus we get the empirical formulas for the temperature dependency of the absorption edges (a) of cuprous oxide:

$$E = a - bT \quad (T > 0^\circ\text{C})$$

where

$$a = 2.083 \text{ eV} \text{ and } b = (3.8 \pm 0.2) \times 10^{-4} \text{ eV/deg};$$

and

$$E = a' - b' \exp(-\theta/T) \quad (T < -50^\circ\text{C})$$

where

$$a' = 2.030 \text{ eV}, \quad b' = 0.012 \text{ eV}, \text{ and } \theta = 280^\circ\text{K}.$$

This value* of θ is that obtained by FRÖHLICH and MOTT¹²⁾ (see subsection (ii) in §5). For the absorption edge (*b*) we get approximately

$$a = 2.92_3 \text{ eV}, \quad b = 3 \times 10^{-4} \text{ eV/deg} \quad (T > 0^\circ\text{C}),$$

and

$$a' = 2.16_2 \text{ eV}, \quad b' = 0.05_0 \text{ eV} \quad (T < -60^\circ\text{C}).$$

It is natural to regard the absorption edge (*b*) as coming from the electronic transition from the filled band to an empty band. The configuration of the three absorption bands existing near the edge (*b*) is, as will be stated later, very similar to that of the energy levels of hydrogen atom, and hence, in harmony with the theoretical expectation, they are interpreted as due to the transition from the filled band to the hydrogen-like states adjoining the lowest state of the empty band. If this interpretation be correct, the limit of convergence of the hydrogen-like levels should give the energy of the lowest level of the empty band, and accordingly the accurate value of the absorption edge (*b*). The results are: 2.148 eV at -80°C and 2.161 eV at -184°C .

It is to be remarked that in the theory of MUTO and ÔYAMA the crystal lattice is assumed to be simple cubic, so that it is impossible to see if the quantitative agreement between theory and experiment—namely, as regards the constants *a*, *b*, *a'*, and *b'*—can be obtained. But the results are none the less important for their mere qualitative agreement with theory, since there has hitherto been no experiment, in which the systematic study of the absorption spectrum extending over a wide range of temperature was carried out.**

It has been pointed out in §3 (ii) that the absorption edge (*b*) has “skirts” on its longer wave-length side, which become more and more intense as the thickness of the sample increases. How far the “skirts” extend, for example in the case of the sample of

* According to the empirical results here obtained, the characteristic temperature of the crystal is to be expected to take the value between 273°K (0°C) and 223°K (−50°C). If we assume, say, $\theta = 250^\circ\text{K}$, we obtain

$$a' = 2.032 \text{ eV}, \quad b' = 0.020 \text{ eV} \quad \text{for the edges (a)}$$

and

$$a' = 2.16_2 \text{ eV}, \quad b' = 0.04_0 \text{ eV} \quad \text{for the edge (b)}.$$

** For instance, FESENFELDT¹³⁾ observed the absorption spectrum of potassium-iodide at no more than four points: 220°, 20°, −186°, and −253°C.

0.1 mm thickness, is shown by the curve (b') in Fig. 5. The curve (b') cannot be expressed either by a linear function or by an exponential function, as has been the case for the curves (a) and (b). It is to be inferred, therefore, that the empty band, strictly speaking the filled band as well, has no discontinuous sharp edge, but its boundary has something like the form shown by the curve in Fig. 10. The form must obviously be the function of temperature. The lowest energy level of the empty band mentioned above corresponds to the point where the curve falls suddenly to enter the "skirts" (shown by the dotted line in the figure).

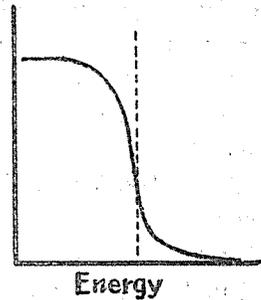


Fig. 10.
"Skirts" on the boundary
of energy band.

§ 5. Interpretation of Absorption Spectrum.

(i) Three absorption bands.

As already stated in §3 (iii), the three absorption bands adjoining the edge (b) have the following features:

- (1) The breadth of each band is ca. 9\AA (0.004 eV) at -80°C and ca. 6\AA (0.002 eV) at -184°C ;
- (2) They are shifted towards longer wave-length with increasing temperature, the energy differences among them being, however, kept constant (see TABLE I).

Now, the breadth of the band in question is smaller than the energy kT at corresponding temperatures, which amounts to 0.017 eV at -80°C and 0.008 eV at -184°C . Hence it is reasonable to consider the three absorption bands as having line- rather than band-character.

According to the theory of the optical absorption of ionic crystal,¹⁴⁾ its absorption spectrum is expected to consist of a hydrogen-like series of absorption lines and a continuous absorption band, which adjoins the series limit. The corresponding series of discrete energy levels are given by

$$E = a - b/n^2, \quad (3)$$

where n is the principal quantum number and b corresponds to

the Rydberg constant in the case of hydrogen atom. Here the energy is measured from the ground state so that a represents the energy of the series limit, which is equal to the energy difference between the ground state and the lowest state of the empty band.

Now, the three absorption lines in question are to be regarded as corresponding to the hydrogen-like states. In fact, the energies of the three absorption lines described in TABLE I can be expressed by the following equations (energies in eV):

$$E = 2.148 - \frac{0.090}{n^2} \quad (\text{at } -80^\circ\text{C}); \quad (4)$$

and

$$E = 2.161 - \frac{0.090}{n^2} \quad (\text{at } -184^\circ\text{C}). \quad (5)$$

In TABLE II the observed values (see TABLE I) and the values calculated from the equations (4) and (5) are given for comparison. The coincidence is excellent.

TABLE II. *Hydrogen-like states (energies in eV)*

n	-80°C		-184°C	
	From (4)	Observed	From (5)	Observed
1	2.058		2.071	
2	2.125	2.125	2.138	2.137
3	2.138	2.138	2.151	2.151
4	2.142	2.142	2.155	2.155
⋮				
∞	2.148		2.161	

Now, it is forbidden¹⁵⁾ for an electron to be excited from the ground state (filled band) to the lowest state of "conducting states" by absorption of light in a crystal with simple cubic lattice, where by the conducting states are meant the states containing not only the electronic states in the empty band, but also the hydrogen-like states. It is, therefore, forbidden for an electron to be excited from the ground state to the lowest state ($n=1$) of the hydrogen-like states. The crystal lattice of cuprous oxide is not, indeed, simple cubic, but such that copper ions form the face-centered cubic lattice and oxygen ions the body-centered cubic lattice. But,

if the same selection rule is assumed to hold also in this case, the absorption line due to the transition from the ground state to the state $n=1$ will not be observed. This is actually the case, since the absorption line corresponding to the energy of the state $n=1$ could not be observed, which comes out to be 2.058 eV ($0.602_5 \mu$) at -80°C and 2.071 eV ($0.598_7 \mu$) at -184°C . Thus we have been able to ascertain the existence of the hydrogen-like states adjoining the lowest state of the empty band as expected by the theory.

(ii) Two sharp absorption edges (a).

As mentioned in §3, the energy difference between the two absorption edges (a) keeps a *constant* value (0.028 eV or 226 cm^{-1}) as the temperature changes, the fact which indicates the existence of a doublet level, whose separation is 226 cm^{-1} .

The electronic state qualified for the filled band of cuprous oxide is obviously either $(3d)^{10}$ of Cu^+ or $(2p)^6$ of O^{--} . Now, the ground states of the ions, formed when Cu^+ and O^{--} are deprived each of one electron, are known to be doublets; namely, $(3d)^9 \cdot {}^2D$ for Cu^{++} and $(2p)^5 \cdot {}^2P$ for O^- . Hence, if the observed doublet separation could be found to be equal to that of 2D (or 2P), it might be inferred that the filled band of cuprous oxide should be due to Cu^+ (or O^{--}).*

The doublet separation (${}^2D_{3/2} - {}^2D_{5/2}$) of Cu^{++} amounts to -2061 cm^{-1} ,** while the separation of the ground state 2P of O^- is as yet unknown. The rough estimation of the doublet separation of O^- can, however, be made from that of halogen atom, whose electronic configuration is the same as that of O^- . As will be seen in TABLE III, the doublet separation of the ground state of halogen atoms decreases with atomic number. Since O^- is isoelectronic with F_1 but has smaller atomic number than F_1 , it may safely be inferred that the doublet separation of O^- should be smaller than 400 cm^{-1} (0.049 eV).

* This consideration comes from MOTT,¹⁶⁾ who pointed out that the so-called first peak of absorption appearing at the long wave-length tail of the characteristic absorption band of alkali-halides manifests itself as a doublet, and that its separation is nearly equal to that of the neutral halogen atom; the halogen atoms exist as "impurity" in the alkali-halide crystal, whose filled band is due to the singly charged negative ion of halogen.

** This is the value calculated by the writer from the result obtained by L. BLOCH and E. BROCH¹⁷⁾ in their study on the emission spectrum of copper in the ultra-violet region.

TABLE III. Doublet separation of the ground state of halogen atoms¹⁸⁾

Z		Electronic configuration	${}^2P_{1/2} - {}^2P_{3/2}$
9	Fr	K (2s) ² (2p) ⁵	- 407.0 cm ⁻¹
17	Cl	K L (3s) ² (3p) ⁵	- 881.
35	Br	K L M (4s) ² (4p) ⁵	-3685.
8	O ⁻	K (2s) ² (2p) ⁵	?

Now, the separation of the doublet in question is 226 cm⁻¹ (0.028 eV). It is therefore a natural consequence that the doublet in question is to be identified with that of O⁻ and, accordingly, the filled band of cuprous oxide is to be regarded as due to the electronic state (2p)⁶ of O⁻.

The filled band of cuprous oxide has hitherto been ascribed to the electronic state (3d)¹⁰ of Cu⁺, and that for the following reasons: 1) The first peak of the ultra-violet absorption of transparent oxides, e.g. BeO, is expected to appear at the wave-length region of the order 1,000 Å. Since, however, in the case of cuprous oxide strong absorption appears in the visible region, it is assumed that, while the ground state of transparent oxide is due to the 2p-band of O⁻, the ground state of cuprous oxide is the 3d-band of Cu⁺, which is supposed to lie above the 2p-band of O⁻.¹⁹⁾

2) From measurement of Hall coefficient it has been confirmed that the electric conductivity of cuprous oxide is to be attributed to the drift of positive holes. The positive holes are brought into existence by the transformation of either Cu⁺ into Cu⁺⁺ or O⁻ into O⁻. But, since copper is normally bi-valent, it seems more probable that positive holes are created by copper ions.²⁰⁾

According to the investigation of X-ray emission band of some oxides (BeO, MgO, etc.), the K-spectrum of oxygen must be interpreted as to correspond to the transition from the 2p-band to the K-level, and from the study of the shape of the short wave-length tail of the spectrum it is concluded that the effective mass of the positive hole situated in close vicinity to the highest level of the 2p-band must be considerably smaller than that of free electron.²¹⁾ ENGELHARD,²²⁾ on the other hand, studied the temperature depend-

ency of the mobility and the mean free path of positive holes on cuprous oxide, and his results analysed by FRÖHLICH and MORR²³⁾ yielded for the values of characteristic temperature and effective mass of positive hole 280°K* and 0.25 m (m represents the mass of free electron) respectively. That the effective mass is very small means that there are positive holes in the vicinity of the highest level of the filled band. On the basis of these facts, MORR and GURNEY²⁴⁾ entertain serious doubts about the hypothesis that the filled band of cuprous oxide is due to the electronic state $(3d)^{10}$ of Cu^+ . The present writer's results seem to lend support to MORR and GURNEY's view.

By extrapolation of the curves (α) in Fig. 5 (§3) we get, for the energies of the two absorption edges (α) at 0°K, 2.032 eV and 2.004 eV.** It is worthy of notice that these values coincide, within the error estimated, with the value of electron affinity A of oxygen atom: (2.2 ± 0.2) eV, which was determined by LOZIER²⁵⁾ for the first time by a direct method. It is generally accepted that there is no electronic state with negative energy, which belongs to negative ion, other than its ground state.²⁶⁾ Hence the capture of an electron by a neutral atom will give rise to a continuous spectrum (i.e. the so-called electron affinity spectrum) extending indefinitely to the shorter wave-length side from an edge, whose wave-length is given by

$$\lambda = \frac{hc}{A}.$$

The ground state of O^- is a doublet ${}^2P_{1/2}$ and ${}^2P_{3/2}$, so that the electronic transition therefrom to the continuous level of positive energy through absorption of light will give rise to an affinity spectrum in absorption, of which the absorption edges just correspond to the ionization energy or the electron affinity A . Taking this interpretation for granted, we arrive at the conclusion that the absorption with the edges (α) is nothing but the electron affinity spectrum of oxygen atom.

(iii) A new absorption band.

As regards what is revealed by the new absorption band stated

* See pp. 119 and 120.

** Small corrections must be made to these values if the zero-point energy of lattice vibration is taken into account. But it is neglected in the present discussion.

in subsection (iv) of §3, the writer is of the opinion that the empty band must be composed of at least two parts separated from each other. It is to be reminded that in their study on the secondary electron emission of some ones (Cu_2O , etc.) of ionic crystals BRUNING

and DE BOER²⁷⁾ suggested the splitting of the empty band, which is in accord with the writer's opinion.

The interpretations given in this article are illustrated by the scheme of electronic levels given in the annexed figure (Fig. 11).

§ 6. Summary.

Owing to the success in preparing a very thin sample of cuprous oxide and in constructing special absorption tubes, the writer could study its absorption spectrum at various temperatures down to liquid air temperature.

The main results obtained are as follows:

- 1) The spectrum revealed three absorption edges, three absorption lines, and an absorption band;
- 2) The existence of hydrogen-like states expected by theory was ascertained;
- 3) The temperature dependency of the absorption edges is in harmony with the theoretical expectation;

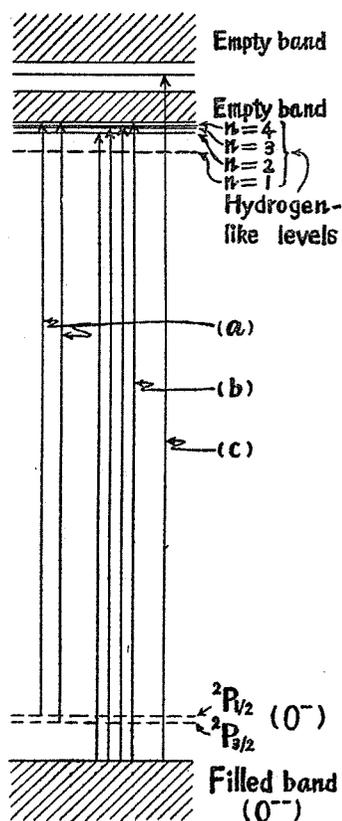


Fig. 11.

Electronic levels of cuprous oxide.

- 4) The two absorption edges, forming a doublet, arise from the impurity levels due to the 2P -state of O^- ;
- 5) The filled band of cuprous oxide corresponds in all probability to the electronic state $(2p)^6$ of O^{2-} ;
- 6) The absorption with doublet edges is to be interpreted as the electron affinity spectrum of oxygen atom;

- 7) The empty band consists of two parts, separated from each other.

In conclusion, the writer wishes to express his sincere thanks to Prof. T. HORI, the director of the Institute of Low Temperature Science of Hokkaidô University, for his continued interest in this work and the many valuable suggestions he made during the investigation and also for his kindness in revising the original manuscript, and further to Asst. Prof. K. KATSUKI, Muroran College of Technology, who has helped the writer in preparing the sample. Finally, the writer is indebted to Educational Ministry for financial aid.

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