<sup>4</sup>Gol'din, Tret'yakov, and Novikova, U.S.S.R. Acad. Sci. Session on Peaceful Uses of Atomic Energy, July 1955.

<sup>5</sup>B. Zajac, Phil. Mag. **43**, 264 (1952).

Translated by J. G. Adashko 285

## INVESTIGATION OF THE X-RAY SPECTRA OF THE SUPERCONDUCTING COMPOUND CuS

## I. B. BOROVSKI I and I.A. OVSYANNIKOVA

Institute of Metallurgy, Academy of Sciences, U.S.S.R.

Submitted to JETP editor June 16, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) 37, 1458-1460 (November, 1959)

N the formation of a chemical compound there is always a rearrangement of the electron energy spectrum of the elements that enter into the composition. These changes are accurately determined from the fine structure of the x-ray emission and absorption spectra.

In the case of superconducting compounds of nonsuperconducting elements, according to the presently developing concepts,<sup>1</sup> the fine structures of the x-ray spectra of the metals will change so as to come closer to the fine structures of the spectra of a superconducting metal, whose position in the periodic table is close to that of the metal under consideration (in the same period).

We report in the present paper the results of an investigation of the fine structure of x-ray absorption and emission K spectra of sulfur and copper in the pure elements and in the compound CuS. These results confirm the foregoing point of view. Sulfur and copper are nonsuperconducting elements, while CuS is a superconductor with a transition temperature 1.62°K. The CuS lattice is of space group  $D_{6h}^4$  (reference 2). The investigations were carried out in an x-ray vacuum spectrograph with bent quartz crystal (radius of curvature 500 mm, Kapitza-Johann focusing). Photographic registration was used. The sulfur spectra were obtained in reflection from the  $(10\overline{11})$  plane, those of copper from the  $(13\overline{40})$  plane. The accuracy of measurement of the position of the sulfur edge was 0.4 xE, that of copper - 0.15 xE, and that of the positions of the maxima of the emission lines of sulfur was 0.2 xE. The emission K spectrum of sulfur was studied by a secondary method.

The diagram shows the average microphotograms of the resultant spectra; the curves are arranged in such a way that the inflection points of the long-wave portion of the S and Cu edges coincide in the CuS. This point, accurate to the width of the initial state, determines the position of the Fermi surface of the energy spectrum of the compound. All the curves that represent the fine structures of the spectra are arranged about this point in equal energy scale.

The experimental results obtained allow us to note the following (see table):

1. The sulfur spectrum in CuS does not have a discontinuity between the center of the short-wave branch of the last emission line and the point of in-flection of the long-wave portion of the edge. This corresponds to a metallic character of the conductivity of the CuS compound.

2. In the absorption spectrum of the sulfur in CuS a maximum, which is new compared with the spectrum of pure sulfur, appears for the absorption coefficient in the long wave portion of the edge abc (see diagram).

3. The intensity ratio  $J_{\beta_X}/J_{\beta_1}$  of the sulfur spectrum in the CuS is reduced to one half the value in the pure sulfur spectrum.

4. The absorption edge of copper in CuS has lost completely the fine structure that is characteristic of the edge of pure copper. The form of the edge exhibits great similarity with the K edge of Zn or Ga.

5. There is a similarity in the form of the Cu and S edges in CuS (the maxima of the absorption coefficients A and A' or B and B' are located at approximately equal distances from the point F; the regions def and d'e'f' have the same

Fine-structure element	In the pure element		In the compound		Shift
	хE	ev	хE	ev	$\Delta \lambda$ , ev
Start of sulfur absorption edge Maximum of $K\beta_1$ sulfur line Maximum of $K\beta_x$ sulfur line Start of copper absorption edge Maximum of $K\beta_5$ copper line Maximum of $K\beta_1$ copper line	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} 2470.1\\ 2464.3\\ 2467.3\\ 6515.1\\ 6512.8\\ 6405.7\end{array}$	5012.4 5021.6 5013.4 1377.55 1378.20 1389.26	2467.92463.42467.46516.96513.96904.3	-2.2-0.9-0.1+1.8+1.1+3.6

Wavelengths of different elements of the fine structure



Dependence of the emission-line intensity J and of the coefficient of mass absorption  $\mu/\rho$  on the wavelength: a-spectra of Cu: curve 1-copper metal, curve 2-copper in CuS; b-spectra of sulfur in CuS; c-spectra of pure sulfur. The emission lines are shown shaded. The energy scale is 0.86 ev per division, corresponding to 0.13 xE in the region of wavelengths of the copper edge and to 1.74 xE in the region of wavelengths of the sulfur edge.

curvature relative to the abscissa axis).

6. An investigation of the  $K\beta_1$  line of copper by the ionization method has shown that the spectrum of metallic copper has a satellite  $K\beta'$ , which is absent from the spectrum of copper in CuS, or from the spectrum of Zn.

The following is a possible interpretation of the results obtained: the electron configuration of copper (free atoms) is  $3s^23p^4$ . The shortest emission lines of sulfur,  $K\beta_1$  and  $K\beta_x$ , are due to transitions of electrons from the filled portion 3p of the band to the 1s level. The reduction in the intensity of the  $K\beta_x$  line of the S spectrum in CuS and the appearance of an additional long-wave structure in the absorption spectrum are evidence that in the CuS compound a portion of the 3p electrons of the sulfur has gone over to a different state, making it possible to excite electrons in previouslyoccupied states. The absorption spectrum of copper in the compound has changed in a way as to approach the zinc spectrum. It follows from this that on the average one sulfur electron has gone

from the 3p state to the 4s state of copper. Actually this electron belongs to the conduction band of the entire compound, with metallic properties, the same as the "proper" 4s electron of copper, given up by each copper atom to the conduction band. The structure of the ionic residue of copper is  $3d^{10}$ . The absence of a satellite  $K\beta'$  in the spectrum of copper in CuS is an additional argument in favor of the above.

In light of these facts, it becomes necessary to revise the structure of covellin,<sup>3</sup> which is considered an ionic type compound. X-ray-spectral data indicate that CuS is a compound of the intermetal-lic type, in which the atoms of both components give up electrons to the conduction band. This agrees with the physical properties of CuS — metallic character of conductivity and diamagnetism.

<sup>1</sup> I. B. Borovskii, Тр. инст. металургии АН СССР, (Trans. Inst. of Metallurgy, Acad. Sci. U.S.S.R.), vol. 6. U.S.S.R. Acad. Sci. 1959.

<sup>2</sup> Strukturberichte, Leipzig, 2, 10, 229 (1937). <sup>3</sup> N. V. Belov, Структуры ионных соединений и металлических фаз, (<u>Structures of Ionic Compounds</u> <u>and Metal Phases</u>), U.S.S.R. Acad. Sci. 1947.

Translated by J. G. Adashko 286

## ANGULAR DISTRIBUTIONS OF ALPHA PARTICLES FROM THE REACTION $C^{12}$ (p, p'3 $\alpha$ )

- S. S. VASIL'EV, V. V. KOMAROV, G. V. KOSHE-LYAEV, and A. M. POPOVA
  - Institute of Nuclear Physics, Moscow State University

Submitted to JETP editor July 3, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) 37, 1460-1461 (November, 1959)

We investigated the angular distributions of  $\alpha$ particles that result from the decay of C<sup>12</sup>, induced by fast protons with energies  $22 \pm 1$  and  $29 \pm 1$  Mev. The decay of the C<sup>12</sup> nuclei was observed in the form of five-pronged stars (three  $\alpha$  particles and the incident and scattered protons), formed in nuclear photoemulsions Ya2 and D-NIKFI, bombarded by protons in the proton synchrotron of the Research Institute for Nuclear Physics of the Moscow State