

J. PHYS. SOC. JAPAN 36 (1974) 311

Optical Absorption of CuFeS_2 and Fe-Doped CuAlS_2 and CuGaS_2

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(Received October 17, 1973)

Chalcopyrite, CuFeS_2 , has been known as an antiferromagnetic semiconductor. As the nonmagnetic analogues of CuFeS_2 there are some I-III-VI₂ ternary semiconductors. For chalcopyrite which contains magnetic ions Pauling and Brockway¹⁾ considered that CuFeS_2 is a mixture of two extreme ionic states, $\text{Cu}^+\text{Fe}^{3+}\text{S}_2^{2-}$ and $\text{Cu}^{2+}\text{Fe}^{2+}\text{S}_2^{2-}$.

The optical absorption edge of chalcopyrite²⁾ lies at much lower energy than those of nonmagnetic analogues, CuAlS_2 and CuGaS_2 , lie.³⁾ It is naturally expected that d-electrons take part in this optical absorption. In order to clarify the origin of this low absorption edge and to get some informations of the ionic state of CuFeS_2 we performed optical absorption measurements on the evaporated film of CuFeS_2 and single crystals of non-magnetic compounds, CuAlS_2 and CuGaS_2 , which were doped

with the magnetic ion, Fe, in various concentrations.

These crystals were prepared by the chemical transport reaction in the closed tube, using iodine as a transport agent. Absorption spectra of $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$ are shown in Fig. 1 together with those of CuFeS_2 and CuAlS_2 . CuFeS_2 shows the absorption edge at about 0.6 eV. Two absorption peaks are observed at 1.3 eV and 2.0 eV on the lower energy region of the absorption edge of Fe-doped CuAlS_2 . For $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ similar two absorption peaks also occur at 1.2 eV and 1.9 eV. The absorption coefficients of these peaks increase with x, and the oscillator strength is about $7 \cdot 10^{-2}$.

In Cu-doped ZnS, which is a binary analogue of CuGaS_2 , the charge transfer transitions from Cu^{2+} were observed in the same energy region.⁴⁾ However, we can say that Cu^{2+} ions do not participate in the absorption peaks which are observed for Fe-doped CuAlS_2 and CuGaS_2 from the following two optical investigations.

We made single crystals of $\text{CuAl}_{1-x}\text{M}_x\text{S}_2$ and $\text{CuGa}_{1-x}\text{M}_x\text{S}_2$, where M was Mn or Zn ion. Mn and Zn are divalent ions and the formation of Cu^{2+} ions is expected by the charge neutrality. Nevertheless the absorption spectra of these crystals show no peaks in the lower energy region of the absorption edge, while Fe-doped CuAlS_2 and CuGaS_2 show these strong absorption peaks.

We also measured the absorption spectrum of an Fe-doped Ga_2S_3 crystal which has the wurtzite structure and contains no Cu ions. It shows similar absorption peaks with those of Fe-doped CuAlS_2 and CuGaS_2 in the same energy region.

From these results it is concluded that strong absorption bands of $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$ at 1.3 eV and 2.0 eV and of $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ at 1.2 eV and 1.9 eV are not related to the presence of Cu ions and originate from Fe^{2+} ions. The large value of oscillator strength suggests that these absorptions arise not from the d-d transition but from the charge transfer transitions relating to Fe^{2+} . Then, it is highly probable that the absorption edge of CuFeS_2 at about 0.6 eV is the foot of the corresponding transition.

Details will be published elsewhere.

References

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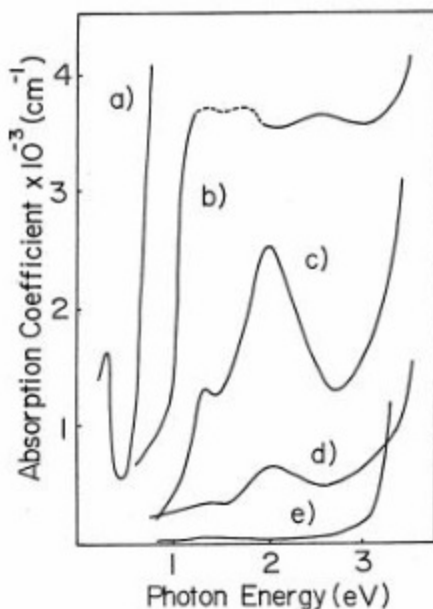


Fig. 1. Absorption spectra of a) CuFeS_2 , b) $\text{CuAl}_{0.93}\text{Fe}_{0.07}\text{S}_2$, c) $\text{CuAl}_{0.95}\text{Fe}_{0.05}\text{S}_2$, d) $\text{CuAl}_{0.995}\text{Fe}_{0.005}\text{S}_2$ and e) CuAlS_2 .

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