Optical Absorption of CuFeS	extsubscript{2} and Fe-Doped CuAlS	extsubscript{2} and CuGaS	extsubscript{2}

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Chalcopyrite, CuFeS	extsubscript{2}, has been known as an antiferromagnetic semiconductor. As the nonmagnetic analogues of CuFeS	extsubscript{2}, there are some I-III-VI	extsubscript{2} ternary semiconductors. For chalcopyrite which contains magnetic ions Pauling and Brockway	extsuperscript{1} considered that CuFeS	extsubscript{2} is a mixture of two extreme ionic states, Cu\textsuperscript{2+}Fe\textsuperscript{3+}S\textsubscript{2} and Cu\textsuperscript{2+}Fe\textsuperscript{3+}S\textsubscript{2}.

The optical absorption edge of chalcopyrite	extsuperscript{1} lies at much lower energy than those of nonmagnetic analogues, CuAlS\textsubscript{2} and CuGaS\textsubscript{2}. It is naturally expected that e-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	extsubscript{2}, we performed optical absorption measurements on the evaporated film of CuFeS\textsubscript{2} and single crystals of non-magnetic compounds, CuAlS\textsubscript{2} and CuGaS\textsubscript{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 CuAl\textsubscript{1−x}Fe\textsubscript{x}S\textsubscript{2} are shown in Fig. 1 together with those of CuFeS\textsubscript{2} and CuAlS\textsubscript{2}. CuFeS\textsubscript{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\textsubscript{2}. For CuGa\textsubscript{1−x}Fe\textsubscript{x}S\textsubscript{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 7.10⁻².

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

We made single crystals of CuAl\textsubscript{1−x}M\textsubscript{x}S\textsubscript{2} and CuGa\textsubscript{1−x}M\textsubscript{x}S\textsubscript{2}, where M was Mn or Zn ion. Mn and Zn are divalent ions and the formation of Cu\textsuperscript{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\textsubscript{2} and CuGaS\textsubscript{2} show these strong absorption peaks.

We also measured the absorption spectrum of an Fe-doped Ga\textsubscript{2}S\textsubscript{2} crystal which has the wurtzite structure and contains no Cu ions. It shows similar absorption peaks with those of Fe-doped CuAlS\textsubscript{2} and CuGaS\textsubscript{2} in the same energy region.

From these results it is concluded that strong absorption bands of CuAl\textsubscript{1−x}Fe\textsubscript{x}S\textsubscript{2} at 1.3 eV and 2.0 eV and of CuGa\textsubscript{1−x}Fe\textsubscript{x}S\textsubscript{2} at 1.2 eV and 1.9 eV are not related to the presence of Cu ions and originate from Fe\textsuperscript{3+} 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\textsuperscript{3+}. Then, it is highly probable that the absorption edge of CuFeS\textsubscript{2} at about 0.6 eV is the foot of the corresponding transition.

Details will be published elsewhere.

References

1) L. Pauling and L.O. Brockway: Z. Krist. 82 (1932) 188.