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Photoconductivity Spectrum of MnS

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Photoconductivity spectra of thin single crystals of MnS were measured.

Transparent green crystals with 1 mm triangular sides and 10μm thickness were obtained by iodine transport reaction. Samples for photoconduction measurements were prepared by evaporating gold onto the top surfaces of the crystals as electrodes. The electrode spacing was typically 0.1 mm long. The resistance of the sample thus prepared was about 1 megohms at room temperature.

The light from a Bausch-Lomb high intensity monochromator with a 42 Watt halogen light source was chopped mechanically at 187.5 Hz and was used to illuminate the sample. The photocurrent was detected by a PAR model-HR8 Lock-in amplifier. The observed photocurrent was rather small with its maximum value of order 5×10^{-11} Amps at 100 V/cm d.c. field (at peak 1).

Typical result of relative-sensitivity (ratio of photocurrent to light intensity) spectrum measured at room temperature is illustrated in Fig. 1 and the absorption spectrum is also shown in the same figure. The photocurrent decreased with decreasing temperature so that low temperature spectrum could not be obtained.

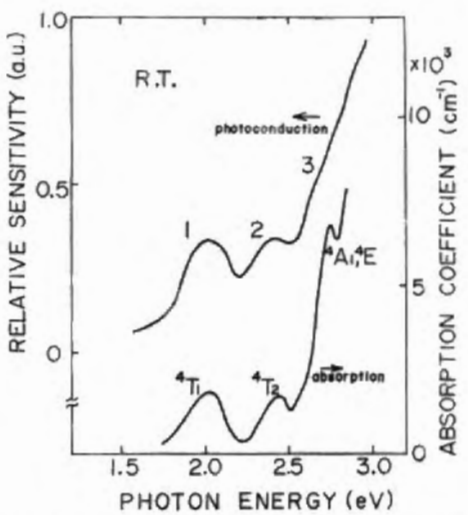

Fig. 1. Photoconductivity and absorption spectra of MnS.

Two prominent peaks 1, 2 and a sharp rise 3 were found in the spectrum. The sharp rise 3 probably corresponds to the absorption edge of the crystal. It is very interesting that the photoconduction peaks 1 and 2 appear at the same energy position where crystalline field absorption peaks of Mn^{2+} occur.[1] The peak 1 corresponds to $^6A_1-{}^4T_1$ and peak 2 to $^6A_1-{}^4T_2$.

With the aid of He-Ne laser (1.96 eV), it was confirmed that photocurrent at peak 1 was approximately proportional to the incident light intensity by two orders of magnitude.

Photoconduction due to crystalline field transition of Co^{2+} in ZnO was already reported by Kanai.[2] Similar photoconduction effects have been observed in epitaxially grown MnO film where crystalline field transition of Mn^{2+} causes photoconduction.[3]

As the excited states of $(3d)^n$ configuration themselves do not contribute to an electric conduction, following mechanisms can be postulated as the cause of photoconduction through crystalline field transition.

(1) A Frenkel exciton formed by crystalline field transition produces free carriers either through exciton-exciton collision or exciton-impurity collision. (Here 'impurity' includes crystalline imperfection.) The former possibility is excluded because the observed photoconduction at peak 1 was a linear function of the light intensity as mentioned above. In the latter case an exciton transfers its energy to an electron (hole) located at the 'impurity' and the electron (hole) will migrate in the conduction (valence) band. This mechanism is possible because even the purest sample obtained by the chemical transport may contain considerable amount of halogen impurity.

(2) Recent measurement of soft X-ray photoemission by Langer *et al.*[4] claims that $(3d)^5$ level of Mn^{2+} in ZnS. as well as one in MnS, lies about 2 eV below the top of the valence band. If this is the case, the 3*d* level may form a quasi-localised state and there is a possibility that this explains the observed photoconduction.

There has been no decisive experiment to determine whether (1) or (2) is the case, so that no conclusive remarks can be given.

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