Electron Spin Resonance Studies of Fe in CuGaSe₂

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ESR spectra (X band) were measured in single crystals of CuGaSe₂ prepared by traveling heater method (THM) and iodine transport (IT) technique. In the THM-crystal an anisotropic signal around 200-300 mT, which is completely quenched by H₂-annkealing, is assigned to Fe²⁺. On the other hand, two types of ESR spectra were observed in IT-crystals. In the type-1 spectrum, nearly isotropic lines were found at 110-130, 400 and 890-950 mT. The spectral features are similar to that of Fe³⁺ in CuInSe₂. On the contrary, in the type-2 spectrum, a strongly anisotropic resonance line was observed and was assigned to Fe⁴⁺ states. Annealing in Se vapor completely quenches the type-2 signal but results in appearance of the type-1 spectrum. This finding may be explained by an assumption that the Fermi level is lowered below the Fe²⁺/Fe³⁺ demarcation level by reduction of Se-vacancy brought about by the Se-vapor anneal.

KEY WORDS: CuGaSe₂ single crystals, electron spin resonance, iron impurity

1. Introduction
Iron has been known as a dominant impurity species in chalcopyrite type crystals.¹ From previous optical and ESR studies it has been elucidated that Fe in CuAlS₂,²³ CuGaS₂,⁴ CuInS₂,⁵ CuAlSe₂,⁶ and CuInSe₂⁷ becomes both divalent and trivalent depending on the position of Fermi level relative to the demarcation level delineating the boundary between Fe²⁺ and Fe⁴⁺. Some of the Fe impurities are known to form defect-complexes combined with some sort of vacancies or unknown impurity species.⁸ Despite long history of studies, only a few ESR data are available for Fe impurity in CuGaSe₂. This is the motivation of the present study.

2. Experimental
Samples were single crystals of CuGaSe₂ prepared by traveling heater method (THM) and by chemical transport reaction using iodine as a transporting agent (hereafter referred to as IT). The THM crystal was supplied by Mie University.⁹ The IT technique provided platelet-shaped single crystals. ESR spectra were measured using JEOL type JES-RE2X X-band spectrometer. Temperature of measurement was controlled between 4 and 60 K.

3. Results and discussion
ESR spectra of the THM crystal are plotted in Fig.1 for different angles between the magnetic field and the crystal orientation. A narrow isotropic line I at g=2.006 and an anisotropic signal A, which varies between g=2.2 and 3.3 are observed. The intensity of the isotropic signal I is increased by H₂-annealing (producing V₅e donor) but decreased by O₂-annealing (reducing V₅e), from which the signal is assigned to V₅e. Details for this signal has been described elsewhere.⁰ On the other hand, the anisotropic signal A may be associated with Fe impurity, since the signal showing the similar angular dependence in CuInSe₂ was associated with Fe impurity.⁷ Both H₂- and O₂-annealing completely quench the signal A. The H₂-annealing produces V₅e, so that the Fermi level of the annealed sample may be pushed up above the Fe²⁺/Fe³⁺ demarcation level changing the Fe valence from Fe³⁺ to Fe²⁺. This can explain the disappearance of Fe³⁺-related ESR signal. The reduction of the signal A by O₂-annealing may be explained if the signal is caused by Fe³⁺-V₅e complex, since O₂-annealing is thought to reduce V₅e.

On the other hand, two types of ESR spectra associated with the Fe impurity were observed in IT crystals. Some of the IT crystals showed a spectrum (Type 1) as plotted in Fig.2. The crystal was rotated around the <110> axis. In this spectrum several anisotropic lines denoted as B were found at 110-130 mT, 400-430 mT and 900-950 mT. The spectral feature is similar to that of Fe³⁺ in CuInSe₂. Fe-X complex different from...
Those in THM crystal may be involved.

Another type of ESR spectrum (type 2 spectrum) as shown in Fig. 3 was observed in some of the IT crystals. In this spectrum, ESR lines marked as C was observed, whose resonance field varied strongly with the direction of magnetic field relative to the crystal orientation. A resonance line I due to V_{Se} similar to that observed in THM crystal was observed.

Similar anisotropic signal was reported in CuAlS_{2} and was assigned to Fe^{2+} states. The ESR signal was attributed to the microwave transition within the lowest Ms=±2 non-Kramers doublet of the Fe^{2+}. The angular-dependence of Fe^{2+} signal was theoretically analyzed and found to obey a 1/cosθ relation. The signal-C is plotted by closed circles as a function of the angle θ in Fig. 4. The straight curves in Fig. 4 are 1/cosθ functions that provide the best fit to the experimental points. A 4-fold symmetry is observed. Since no 4-fold symmetry exists in the chalcopyrite lattice, the angular dependence suggests existence of two Fe sites with mutually perpendicular 2-fold axes.

Annealing in Se atmosphere completely quenched the signal C and the signal I, but introduced type-1 spectrum. Quenching of the signal I suggests disappearance of the V_{Se} donor, which in turn may introduce a downward shift of the Fermi level E_{F} below the demarcation level delineating Fe^{2+} and Fe^{3+} valence states. This is consistent with our experimental finding that the Fe^{2+} signal disappeared and Fe^{3+}-related signal appeared by Se-annealing.

4. Conclusion

ESR signals due to Fe impurities in CuGaSe_{2} single crystals were investigated. Anisotropic ESR signals were observed in THM and IT crystals, and attributed to Fe-X complex. Strongly anisotropic ESR signal was observed in some of the IT crystal and assigned to Fe^{2+} impurity taking into account the 1/cosθ dependence of the resonance field. This assignment is consistent with the result of the Se-annealing.

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References
