Electron Spin Resonance Studies of Fe in $CuGaSe_2$

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ESR spectra (X band) were measured in single crystals of $CuGaSe_2$ 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 H_2-annealing, is assigned to Fe^{3+}. 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 Fe^{3+} in $CuInSe_2$. On the contrary, in the type-2 spectrum, a strongly anisotropic resonance line was observed and was assigned to Fe^{2+} 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 Fe^{2+}/Fe^{3+} demarcation level by reduction of Se-vacancy brought about by the Se-vapor anneal.

KEY WORDS: $CuGaSe_2$ 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 $CuAlS_2$, [2,3] $CuGaS_2$, [4] $CuInS_2$, [5] $CuAlSe_2$, [6] and $CuInSe_2$ [7] becomes both divalent and trivalent depending on the position of Fermi level relative to the demarcation level delineating the boundary between Fe^{2+} and Fe^{3+}. 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 $CuGaSe_2$. This is the motivation of the present study.

2. Experimental

Samples were single crystals of $CuGaSe_2$ 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 H_2-annealing (producing V_{Se} donor) but decreased by O_2-annealing (reducing V_{Se}), from which the signal is assigned to $V_{Se.}$ Details for this signal has been described elsewhere.[10] On the other hand, the anisotropic signal **A** may be associated with Fe impurity, since the signal showing the similar angular dependence in $CuInSe_2$ was associated with Fe impurity.[7] Both H_2- and O_2-annealing completely quench the signal **A.** The H_2-annealing produces V_{Se}, so that the Fermi level of the annealed sample may be pushed up above the Fe^{2+}/Fe^{3+} demarcation level changing the Fe valence from Fe^{3+} to Fe^{2+}. This can explain the disappearance of Fe^{3+}-related ESR signal. The reduction of the signal **A** by O_2-annealing may be explained if the signal is caused by Fe^{3+}-V_{Se} complex, since O_2-annealing is thought to reduce V_{Se}.

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 Fe^{3+} in $CuInSe_2$.. Fe-X complex different from

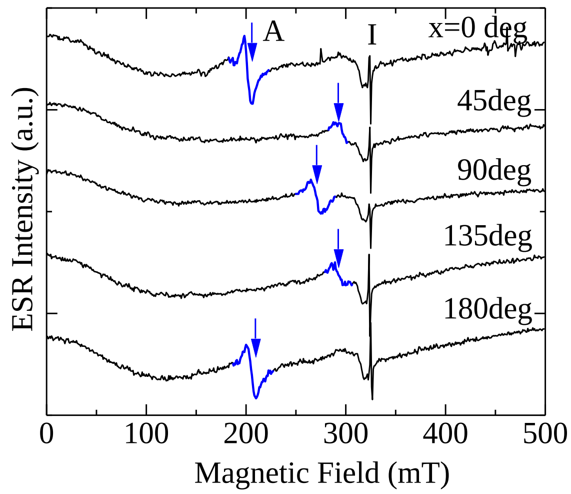

Fig. 1 ESR spectrum of THM-grown $CuGaSe_2$ single crystal .

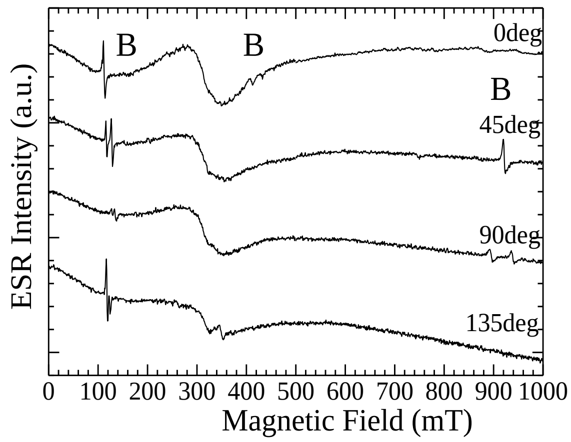

Fig.2 Type 1 ESR spectrum in as-grown IT-CuGaSe2 single

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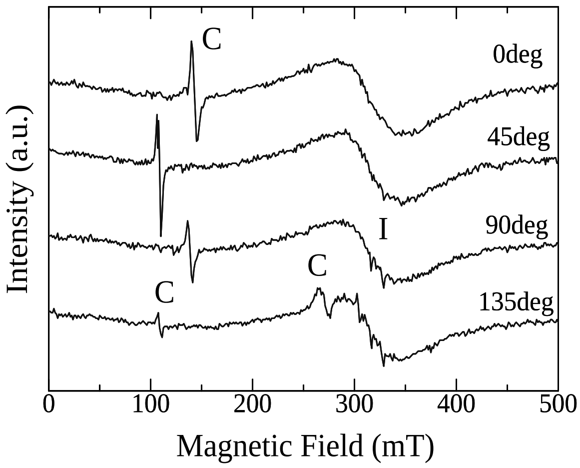

Fig. 3 Type 2 ESR spectrum of an IT-grown CuGaSe2 single crystal

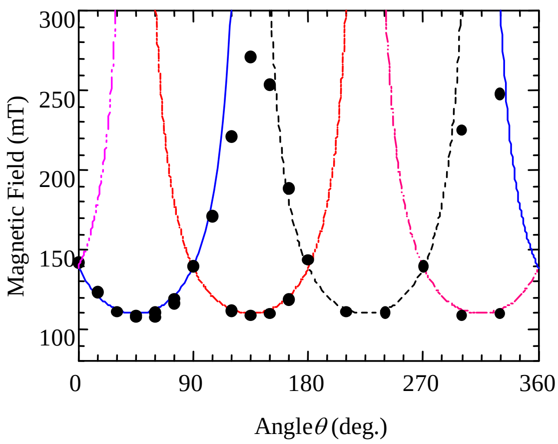

Fig.4 Angular dependence of C line in type 2 $CuGaSe_2$.

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.[11)] The ESR signal was attributed to the microwave transition within the lowest Ms=±2 non-Kramers doublet of the Fe^{3+}. 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.

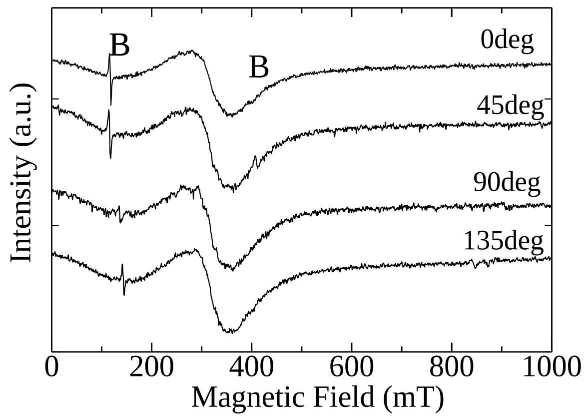

Fig.5 Type 1 ESR spectrum that appears after Se-annealing of as-grown IT-$CuGaSe_2$ which showed Type 2 spectrum

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.

Acknowledgements

This work is supported in part by the New Energy and Industrial Technology Development Organization (NEDO). We express our deep gratitude to Prof. H. Miyake for providing $CuGaSe_2$ single crystals grown by THM technique.

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