

# Electron spin resonance of copper vacancy in CuAlS<sub>2</sub>

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Optically excited electron spin resonance (ESR) spectra of CuAlS<sub>2</sub> single crystals, grown by the chemical vapor transport technique, have been studied at 110–300 K. An isotropic photosensitive ESR signal, consisting of one line at  $g=2.019$ , has been observed. This signal has been attributed to a hole trapped on a copper vacancy with the activation energy, found from the thermal quenching of the ESR signal, being equal to 0.19 eV.

## I. INTRODUCTION

CuAlS<sub>2</sub> semiconductor is the widest band-gap member of I-III-VI<sub>2</sub> ternary compounds, crystallizing in the chalcopyrite structure. With the observation of several strong emissions in green and blue spectral regions from Zn-doped CuAlS<sub>2</sub> crystals having been reported,<sup>1</sup> this compound can be considered as a prospective material for green-to-blue light emitting diode (LED) application.

All as-grown CuAlS<sub>2</sub> has been found to exhibit *p*-type conductivity, which may be tentatively attributed to the native copper vacancies  $V_{\text{Cu}}$  since (1) the as-grown CuAlS<sub>2</sub> crystals have been found by inductively coupled plasma spectroscopy to be highly Cu deficient,<sup>2</sup> and (2) copper vacancies are believed to be formed easily as Cu participates only slightly in the interatomic bonds.<sup>3</sup>

In the present paper we report the direct observation of the electron spin resonance (ESR) signal from a hole trapped on a defect, which is believed to be the copper vacancy.

## II. EXPERIMENTAL

Single crystals were grown by the chemical vapor transport technique from polycrystalline CuAlS<sub>2</sub> compound, which had been prepared by the direct melting of the constituent elements in a BN crucible,<sup>4</sup> with the resulting single crystals being mostly platelike with dimensions of  $15 \times 5 \times 0.5$  mm<sup>3</sup>. ESR spectra were taken with a JEOL JES-RE2X X-band spectrometer at 110–300 K and microwave power of 1–5 mW. Optical excitation of ESR has been carried out by using a 150 mW Xe lamp (white light), as well as a Ritsu MC-10N monochromator (focal length 10 cm, 1200 g/mm grating blazed at 500 nm) in the case of excitation with monochromatic light, the spectral resolution being  $\sim 1$  nm. The ESR excitation spectra were taken at 120 K, each point of the spectrum being obtained after quenching the ESR signal by raising the temperature up to 300 K with subsequent lowering of the temperature down to 120 K to record the signal at each particular wavelength of optical excitation. All spectra were corrected for the spectral response of the optical system.

## III. RESULTS AND DISCUSSION

### A. ESR signal identification

The ESR spectra of as-grown CuAlS<sub>2</sub> crystals, taken in darkness, usually exhibit the signals from the transition atom impurities Cr<sup>2+</sup> and Fe<sup>3+</sup>.<sup>5</sup> The Cr<sup>2+</sup>-related signal shows one highly anisotropic line with  $g_{\parallel}=8.5$ ,  $g_{\perp} \rightarrow 0$ , while the Fe<sup>3+</sup>-related signal consists of five fine structure lines, each of which is split into two components due to the presence of two magnetically inequivalent metal sites in the chalcopyrite lattice of CuAlS<sub>2</sub>.<sup>6</sup> Three out of five Fe<sup>3+</sup> originated fine structure lines are shown in Fig. 1 for the arbitrary orientation of the *c* axis of the crystal in relation to the external magnetic field.

Switching on white light results in the decrease of intensities of Fe<sup>3+</sup>-related lines and in the appearance of a new isotropic *A* signal at  $g=2.019$ , with the peak-to-peak width of about 3 mT, which is shown by the lower curve in Fig. 1. The *A* signal cannot be attributed to the transition metal ion impurities as their ESR spectra are already known to a large extent.<sup>7</sup>

Therefore, we believe that the *A* signal originates from an intrinsic center. Since the observed *g* value of the *A* signal is isotropic and larger than that of a free electron  $g_0=2.0023$ , the signal can be unambiguously attributed to a hole trapped on some highly symmetric center. It is not surprising to observe the isotropic signal from a center in the tetragonal crystal field if we consider (1) the possibility of a defect centered on the less tetragonally distorted sulfur tetrahedron, and that (2) the still remaining small anisotropy of the signal may be further reduced by a thermally stimulated hopping of a hole between four S ions, which results in the detection of an averaged spectrum, as was the case for CuGaS<sub>2</sub>.<sup>8</sup>

Since the linewidth of the *A* signal (3 mT) is quite small, holes trapped either on Cu or Al ions can be excluded as the nuclear moment of Cu leads to a linewidth of about 10 mT for the third hole in the binary analog ZnS,<sup>9</sup> and the nuclear moment of Al is even larger than that of Cu.

Taking into account the above considerations, as well as the Cu deficiency of the CuAlS<sub>2</sub> crystals, discussed in Sec. I, we have attributed the *A* signal to a hole centered on the copper vacancy  $V_{\text{Cu}}$  and equally shared by the four nearest S ions of the anion sublattice. Taking into account the distortion of the chalcopyrite lattice the averaged *g*

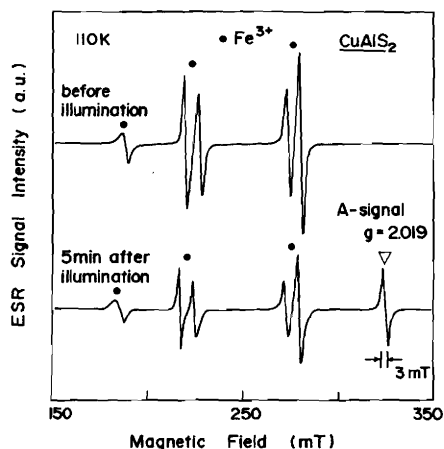


FIG. 1. ESR spectra of the  $\text{CuAlS}_2$  single crystal before and after white light illumination at 110 K and arbitrary orientation of the  $c$  axis of the crystal in relation to the external magnetic field.

factors over four S sites for parallel and perpendicular orientation of the  $c$  axis of the crystal in relation to the external magnetic field can be written in the form<sup>8</sup>

$$\langle g_{\parallel} \rangle = \left[ g_0^2 + \frac{8}{9} g_0 \frac{\lambda}{E} (3 + \tau + \sigma) \right]^{1/2}, \quad (1)$$

$$\langle g_{\perp} \rangle = \left[ g_0^2 + \frac{8}{9} g_0 \frac{\lambda}{E} \left( 3 - \frac{\tau + \sigma}{2} \right) \right]^{1/2}, \quad (2)$$

where  $\lambda$  is the spin-orbit coupling constant,  $E$  is the splitting of the atomic  $^2P_{3/2}$  state of the S ions by the axial electric field of the copper vacancy, and the parameters  $\tau = 2 - c/a$  and  $\sigma = 4X_f - 1$  characterize the distortion of the chalcopyrite lattice from a perfect superstructure of the cubic ZnS lattice.  $X_f$  is a parameter related to the rotation angle of the S-tetrahedra around the cation site, the value of this parameter for the ideal chalcopyrite structure being  $X_f = 1/4$ .<sup>6</sup>

The parameters  $\tau$  and  $\sigma$  for  $\text{CuAlS}_2$  were determined by x-ray diffraction as being equal to 0.042 and 0.072, respectively,<sup>10</sup> while the spin-orbit coupling constant  $\lambda$  can be estimated from the A center in  $\text{ZnS}_x\text{Se}_{1-x}$  as being about  $330 \text{ cm}^{-1}$ .<sup>8,11</sup>

The value of  $E$  is unknown. Considering the experimental  $g$  factor of the A signal the best fit for the  $g$  factors given by Eqs. (1) and (2) has been obtained for  $E = 26000 \text{ cm}^{-1}$  (3.22 eV). Further, the expected anisotropy of the  $g$  factor from Eqs. (1) and (2) is found to be  $\Delta g = \langle g_{\parallel} \rangle - \langle g_{\perp} \rangle = 0.001$ , which falls within the experimental error of our ESR spectrometer.

The value  $E$  of the splitting of the P states of the S ions by the electric field of the copper vacancy has been found to be larger in  $\text{CuAlS}_2$  than that in  $\text{CuGaS}_2$  ( $20500 \text{ cm}^{-1}$ ).<sup>8</sup> This result can be explained if we consider the second shell surrounding the  $V_{\text{Cu}}$  defect in these two compounds, consisting of four Cu cations and eight Al and Ga cations for  $\text{CuAlS}_2$  and  $\text{CuGaS}_2$ , respectively. Since Al-S bonds are more ionic compared with Ga-S ones, the negative electronic charge of S anions, surrounding the copper

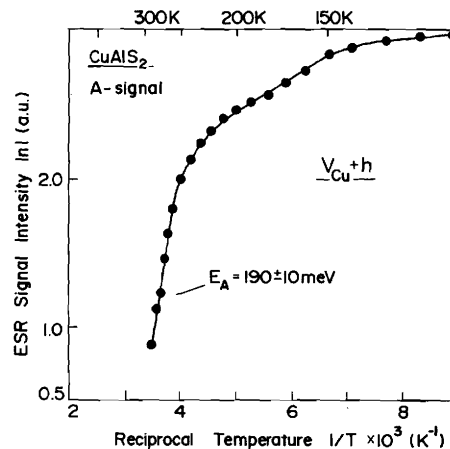


FIG. 2. Thermal quenching curve for the A signal.

vacancy, will be shifted toward this vacancy to a larger extent in  $\text{CuAlS}_2$  than in  $\text{CuGaS}_2$ . Therefore, since the  $p$ -electron shells of the S ions are closer to the copper vacancy in the case of  $\text{CuAlS}_2$ , the electric field of the  $V_{\text{Cu}}$  defect causes larger  $E$  splitting in this compound compared with that in  $\text{CuGaS}_2$ .

## B. Thermal quenching of the A signal

If an energy level, formed by some defect in the band gap of a semiconductor, is not too deep, then the Hartree-Fock approximation may be considered as a good one, and we will have a one-to-one correspondence between energy levels and states of this defect. This is the usual approach used when dealing with "shallow" centers in semiconductors. In the Hartree-Fock approximation the copper vacancy in its empty ( $V_{\text{Cu}}$ ) and filled ( $V_{\text{Cu}} + h \rightarrow V_{\text{Cu}}^0$ ) states can be characterized by the same acceptor level, the ionization energy of which can be deduced from the thermal quenching curves reflecting the process of the thermal emission of captured holes into the valence band.

The thermal emission  $I_{\text{th}}$  of holes is related to the ionization energy  $E_A$  of the energy level by the principle of the detailed balance as

$$I_{\text{th}} = f(T) \exp(-E_A/kT), \quad (3)$$

and, hence, the A signal, formed by holes still captured on the  $V_{\text{Cu}}$  defects, can be written as

$$I(A) = I_0(A) [1 - f(T) \exp(-E_A/kT)], \quad (4)$$

where  $f(T)$  is a slow (as compared with exponential) function of temperature, including the hole capture cross section, the effective density of states in the valence band, and the mean thermal velocity of holes, while  $I_0(A)$  is the intensity of the A signal at  $T \rightarrow 0$ .

Neglecting  $f(T)$  we, therefore, can determine the value of the ionization energy  $E_A$  from the slope of an Arrhenius plot of  $\ln I(A)$  vs  $1/T$ , which is shown in Fig. 2. It should be noted that the value of  $E_A = 190 \pm 10 \text{ meV}$ , found from the thermal quenching curve of the A signal, corresponds within the experimental error to the ionization

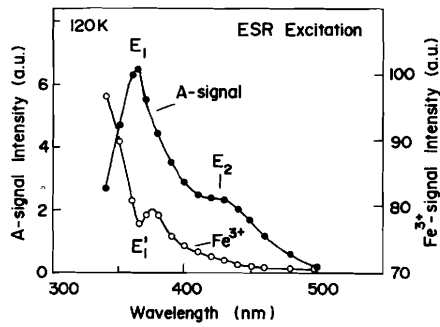


FIG. 3. ESR excitation spectra for the  $A$  signal (●) together with that of the  $\text{Fe}^{3+}$ -related signal (○), taken 10 min after switching on the monochromatic light.

energy  $E_{A'} = 180 \pm 10$  meV of the defect, involved in the purple<sup>12</sup> and violet<sup>2</sup> photoluminescence from the  $\text{CuAlS}_2$  crystals, which has also been attributed to  $V_{\text{Cu}}$ . The last result supports our assignment of the  $A$  signal to a hole trapped by the copper vacancy.

### C. ESR excitation spectra

The excitation spectra for the  $A$  and Fe ESR signals are shown in Fig. 3, each point of the presented curves being taken 10 min after switching on the illumination with monochromatic light. The spectrum for the  $A$  signal exhibits a peak  $E_1$  at 365 nm, as well as a shoulder  $E_2$  at 430 nm, whereas that for the Fe signal shows a local minimum  $E'_1$ , the spectral position of which corresponds precisely to that of the  $E_1$  peak for the  $A$  signal. Therefore, electrons, optically excited from the copper vacancies, are believed to be trapped on the  $\text{Fe}^{3+}$ -related centers, converting them to  $\text{Fe}^{2+}$ .

It is important to note that the sum of the ionization energies for the  $V_{\text{Cu}}$  defect, which were found from the thermal quenching curve for the  $A$  signal (thermal activation of holes into the valence band,  $E_A = 0.19$  eV) and from the ESR excitation spectrum (optical excitation of electron into the conduction band,  $E_1 = 3.40$  eV), corresponds within experimental error to the band-gap energy ( $E_g$ ) of the  $\text{CuAlS}_2$  compound (3.55 eV).<sup>14</sup>

While most of electrons from  $V_{\text{Cu}}$  are excited into the conduction band, some of them are believed to be directly transferred to the deep centers in the band gap, the last process exhibiting itself in the appearance of the  $E_2$  shoulder on the excitation spectrum (Fig. 3). Taking into account the spectral position of the  $E_2$  shoulder (2.90 eV), as well as the activation energy of the  $V_{\text{Cu}}$  acceptor ( $E_A = 0.19$  eV), we can estimate the energy position of the level formed by the deep centers as being  $E_g - (E_2 + E_A) = 0.46$  eV below the minimum of the conduction band. Since neither Fe nor Ni residual impurities can account for the formation of this level as the positions of their energy levels in the band gap are already known,<sup>7</sup> we tentatively assigned the level at  $E_g - 0.46$  eV to either sulfur vacancies ( $V_S$ ) or the Cr impurity ( $\text{Cr}^+/\text{Cr}^{2+}$  energy level).

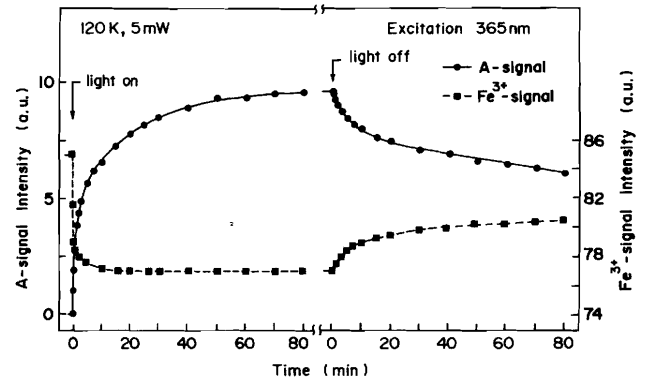


FIG. 4. Changes in the intensities of the  $A$  and  $\text{Fe}^{3+}$  ESR signals after irradiation with 365 nm light.

### D. Time development of the ESR signals

Figure 4 shows the observed changes in the intensities of the  $A$  and Fe signals after irradiation with 365 nm light ( $E_1$  peak on the ESR excitation spectrum). After switching on the light the  $A$  signal appears immediately, rises in intensity as time proceeds, and saturates after 70 min of irradiation. A simultaneous decrease in the intensity of the Fe signal can also be seen, this decrease being faster than the increase in the intensity of the  $A$  signal. The Fe-related signal saturates after 20 min of irradiation at the intensity  $I_{\text{sat}}(\text{Fe}) = I_0(\text{Fe}) - \Delta I_{\text{sat}}(\text{Fe})$ , where  $I_0(\text{Fe})$  is the intensity of the Fe signal before irradiation and  $\Delta I_{\text{sat}}(\text{Fe})$  is the irradiation induced change in the intensity of this signal in saturation.

Switching off the light results in the opposite development, i.e., the intensity of the  $A$  signal decreases and that of the Fe signal increases. The rates of change in the intensities are approximately the same for both signals, the  $A$  signal retaining about 60% of its saturation intensity, and the change in the intensity of the Fe-related signal being about 60% of this value in saturation ( $\Delta I \sim 0.6 \Delta I_{\text{sat}}$ ), even 80 min after switching off the light.

It should be noted that the change in the intensity of the Fe signal can account for only about 80% of that for the  $A$  signal. Therefore, some other defects, in addition to Fe, also take part in the process of trapping of electrons, optically excited from  $V_{\text{Cu}}$  into the conduction band. These defects may be the same ones which are responsible for the appearance of the  $E_2$  shoulder on the excitation spectrum (Fig. 3), although the exact nature of them remains unknown.

### E. Band diagram model

An illustration of the phenomena occurring in the optically irradiated  $\text{CuAlS}_2$  crystal and discussed above is presented in Fig. 5 as a band diagram model. Using this diagram let us discuss consecutively the processes of excitation and trapping of carriers in  $\text{CuAlS}_2$ .

Upon excitation with 365 nm light an electron is emitted from  $V_{\text{Cu}}$  into the conduction band (process 1), which can be written as

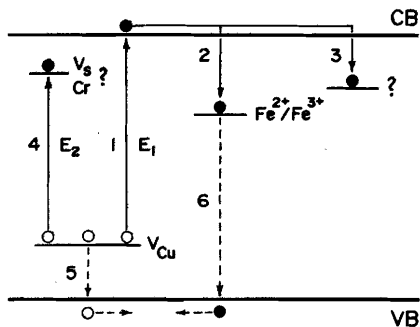


FIG. 5. The proposed mechanism of the optical excitation of electrons from  $V_{Cu}$  into the conduction band (1) with their subsequent trapping by the Fe-related defects (2), as well as by some other unidentified traps (3). The processes of the optical excitation of electrons from  $V_{Cu}$  to the unidentified donors (4), of the thermally induced release of holes from  $V_{Cu}$  into the valence band (5), as well as of the release of electrons from Fe traps (6) with their subsequent recombination with holes released from  $V_{Cu}$  are also shown.



A complementary process for the electron emission (5) is the capture of a hole from the valence band, i.e.,



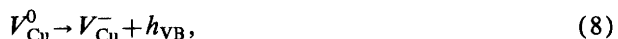
this hole causing the appearance of the  $A$  signal in the ESR spectra. Most of the emitted electrons are subsequently trapped by the Fe-originated traps (process 2), converting  $Fe^{3+}$  into  $Fe^{2+}$ , i.e.,



while some of them ( $\sim 20\%$ ) are trapped on some other unidentified centers (process 3). It should be noted that, since the Fe-related energy levels in  $CuAlS_2$  are very deep (close to the midgap position)<sup>14</sup> and, therefore, the Hartree-Fock approximation is not valid, the Fe-related energy level in Fig. 5 is essentially the demarcation level, denoting ionization energy delineating the charge states  $Fe^{2+}$  and  $Fe^{3+}$ .

While most of electrons from  $V_{Cu}$  are emitted into the conduction band, some of them are directly transferred to the unidentified centers, which may be formed by  $V_S$  or the Cr impurity (process 4), this process causing the appearance of the  $E_2$  shoulder on the ESR excitation spectrum (Fig. 3).

Raising the temperature causes the thermal emission of holes from  $V_{Cu}$  into the valence band (process 5), i.e.,



this process being responsible for the thermal quenching of the  $A$  signal, shown in Fig. 2.

The intensity of the  $A$  signal saturates when the rate of electron emission into the conduction band (process 1)

equals that of the transfer (release) of electrons from the Fe-related traps into the valence band (process 6), with their subsequent recombination with holes, thermally emitted from  $V_{Cu}$ . After switching off the light, the source supplying electrons into the conduction band disappears, and we observe the quenching of the  $A$  signal due to the slow release of electrons from the Fe-related, as well as the other centers, which is shown in Fig. 4.

It would be of interest to study the ESR excitation spectra for the  $Fe^{3+}$ -related signal at the wavelengths of the monochromatic light, corresponding to the energy position of the  $Fe^{2+}/Fe^{3+}$  demarcation level in the band gap of  $CuAlS_2$ , as well as the role of other transition atom impurities, which is planned for the near future.

## IV. CONCLUSIONS

The optically excited ESR spectra of the  $CuAlS_2$  crystals have been studied, the results showing one isotropic photoinduced signal at  $g=2.019$ , which has been assigned to a hole trapped on copper vacancy and equally shared by four surrounding sulfur ions. The activation energy of the  $V_{Cu}$  defect  $E_A=0.19$  eV, deduced from the thermal quenching of the hole-originated ESR signal, agrees well with the results of our previous optical investigations. Electrons, optically excited from  $V_{Cu}$  into the conduction band, have been found to be trapped mainly by Fe-related deep centers, this process exhibiting itself as the decrease in the intensities of the  $Fe^{3+}$  ESR signal.

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