

Optical and ESR Characterization of Transition Atoms in CuAlS_2

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The optical and ESR properties of the CuAlS_2 single crystals, doped with transition atom (TA) elements of the iron group, i.e. Ti, V, Cr, Mn, Fe, Co, and Ni, have been studied. It has been found that TA impurities in the CuAlS_2 host lattice are present in their different valence states, the relative concentrations of these impurities in each valence state being dependent on the position of the Fermi level in the band gap of the host compound in relation to deep energy (demarcation) levels introduced by TA ions.

KEYWORDS: CuAlS_2 ternary semiconductor, transition atom impurity of the iron group, optical absorption spectrum, ESR spectrum, Fermi level

In recent years ternary compounds of the type $\text{A}^1\text{B}^3\text{C}_2^6$, crystallizing in the tetragonal chalcopyrite structure, have been attracting much interest due to their promising luminescent and nonlinear optical properties. CuAlS_2 ternary compound is the widest band gap member of the ternaries, which has been recently found to emit strong green and blue photoluminescence¹⁾ and, therefore, can be considered to be a perspective material for blue and green light emitting device realization.

However, all the as-grown CuAlS_2 crystals have been found to exhibit highly compensated p-type conductivity, which implies that the Fermi level position is located close to the center of the band gap. A defect whose energy is near the center of the band gap will gain or lose electrons as the Fermi level passes through the demarcation level of different charged (valence) states of this defect. The position of Fermi level in the band gap can be influenced by the proper thermal treatments of the crystal, and, if any of the charged states of the defect are paramagnetic, then electron spin resonance (ESR) technique can be used to monitor the motion of the Fermi level in the vicinity of the energy level of the defect.

Since the energy levels, introduced by transition atom (TA) impurities in the band gap of semiconductors (including CuAlS_2), are deep ones, the Hartree-Fock approximation is not valid for TA. Therefore, the TA-introduced energy levels are essentially the demarcation levels, denoting the ionization energy delineating different charged states of the TA ion.

Two types of electronic transitions, related to the TA impurities, can be observed in semiconductors, i.e. 1) d-d transitions among the levels of 3dⁿ-manifold of TA split by the effect of the crystal field, as well as 2) charge transfer transitions, i.e. the electronic transitions from the impurity ion to the ligands or vice versa.²⁾ The charge transfer transitions in ternaries are believed to occur from the valence band of the host compound to the 3d-shell originated orbitals of the TA ion (acceptor-like photoexcitation). The reason for such an interpretation is that the molecular orbitals corresponding to the uppermost valence band states in ternary compounds are composed of

chalcogen 3p orbitals and 3d orbitals of monovalent cations, which makes possible the charge transfer from the ligand orbitals of the valence band to the 3d-shell originated orbitals of TA ion. On the other hand, the molecular orbitals of conduction band for ternaries are composed of 3s orbitals of monovalent and trivalent cations, which makes 3d-shell-conduction band donor-like transitions parity forbidden.

We have tried to determine the type and valence states of TA impurities in the crystals of the CuAlS_2 compound by 1) changing the position of the Fermi level in the band gap by stoichiometry alterations under thermal treatments in different atmospheres or by doping with donor- or acceptor-like impurities and by 2) controlling the resultant change in optical and ESR spectra.

Doping of the CuAlS_2 compound with TA impurities such as Ti, V, Cr, Co, and Ni have been carried out by adding this elements into the starting mixture of the constituent elements used for synthesis of the compound,³⁾ whereas doping with Fe and Mn has been performed during the crystal growth by the CVT.

In Fig. 1 we have summarized the optical absorption spectra of the CuAlS_2 crystals doped with TA impurities. The parameters of the TA ions in CuAlS_2 , for which d-d transitions among the ligand-field split levels of 3dⁿ-manifold have been observed, are listed in Table I, whereas Table II shows the ionization energies of the charge transfer transitions $\text{TA}^{3+} \rightarrow \text{TA}^{2+}$ and $\text{TA}^{2+} \rightarrow \text{TA}^{1+}$, i.e. the position of the demarcation levels in the band gap in relation to the top of the valence band.

The results of the ESR studies are summarized in Table III, showing the *g*-values of TA ions for two orientations of the *c*-axis of the crystal in relation to the external magnetic field, as well as the effective spin values *S'* used in the spin Hamiltonian. The number of fine structure components *N*, observed for TA ions, can be easily deduced from this Table since $N=2S'$.

The valence states (i) of TA ions and the relative concentrations of these ions in each valence state are found to be controlled by the position of the Fermi level in the band gap of the host crystal in relation to the demarca-

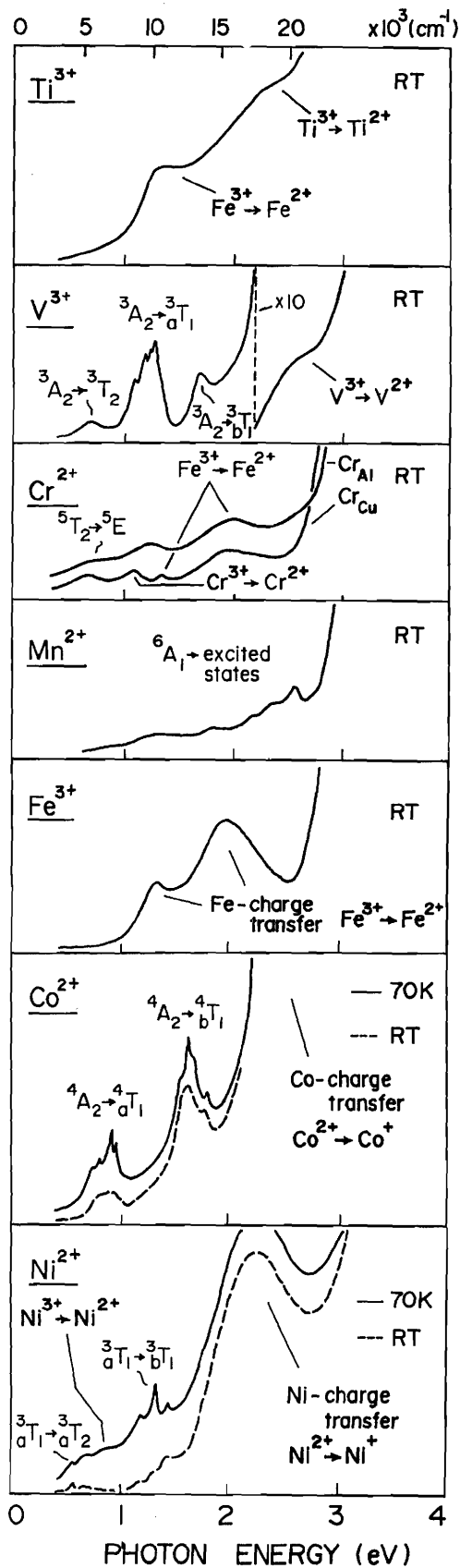


Fig. 1. Compilation of observed optical absorption spectra of TA impurities in CuAlS₂.

tion levels of TA impurities $TA^{i+}/TA^{(i+1)+}$, the position of the Fermi level, in its turn, being dependent on the concentrations of electrically active native and extrinsic

Table I. Spectral positions of the absorption bands baricenters for TA ions in CuAlS₂ host together with the list of parameters of TA ions (in cm⁻¹) in CuAlS₂ in comparison with that for ZnS (given in brackets). The parameters listed include the cubic crystal field parameter Dq , Racah parameter B and the spin-orbit coupling parameter λ .

Conf.	Ion	Energy Transition	Dq	B	λ	Ref.
d ²	V ³⁺	5700 ³ A ₂ → ³ T ₂	570	465	20 ^{a)}	3
		9090 → ³ T ₁	(560)	(465)	(40) ^{a)}	6
		14900 → ³ T ₁ (P)				
d ⁵	Mn ²⁺	17860 ⁶ A ₁ → ⁴ T ₁	580	335		7
		19190 → ⁴ T ₂	(545)	(500)		8
		20890 → ⁴ A ₁ + ⁴ E				
		22420 → ⁴ T ₂				
d ⁷	Co ²⁺	6990 ⁴ A ₂ → ⁴ T ₁	390	575	-185	9
		13280 → ⁴ T ₁ (P)	(375)	(610)	(-195)	10
d ⁸	Ni ²⁺	4530 ³ T ₁ → ³ T ₂	475	460	-250	5
		10350 → ³ T ₁ (P)	(475)	(560)	(-250)	10

^{a)}estimated from ESR data using the expression $g - g_0 = 8\lambda / 10Dq$.

Table II. Ionization energies of TA impurities in CuAlS₂ as compared with that for ZnS¹³⁾ in relation to the top of the valence band.

Transition	Host	Ti	V	Cr	Fe	Ni
2+ → 1+	CuAlS ₂					2.25
	ZnS			2.48		2.46
3+ → 2+	CuAlS ₂	2.38	2.65	1.08	2.0	0.65
	ZnS		2.11	1.0	2.01	0.75
Reference	(CuAlS ₂)	11	3	5	12	5

Table III. The observed g -values for TA ions in CuAlS₂. The lowest line shows the cation site, for which the corresponding TA is believed to substitute.

Conf.	d ¹	d ²	d ⁴	d ⁵	d ⁶	d ⁷	d ⁹		
Ion	Ti ³⁺	V ³⁺	Cr ²⁺	Cr ³⁺	Fe ³⁺	Fe ²⁺	Co ²⁺	Ni ³⁺	Ni ²⁺
S'	1/2	1	1/2	5/2	5/2	1/2	1/2	1/2	1/2
g_{\parallel}	1.902	1.973	8.5	1.998	2.020	2.187	2.138		2.051
g_{\perp}	1.978	1.973	0	1.998	2.020	2.037	2.030	4.38	2.330
Ref.	11, 14	11	4	4	15	16	17	5	5, 18
Site	Al	Cu	both Al and Cu sites				?	?	?

defects, including those formed by TA impurities. Therefore, changing the position of the Fermi level in the band gap by proper thermal treatments, we can observe the redistribution of relative concentrations of TA ions in different charge states, exhibiting itself as the changes in the optical and ESR spectra. As an example, Fig. 2 shows the annealing-induced changes in the ESR spectra of Ni-doped CuAlS₂ crystals.

Taking into account also the observed changes in the optical spectra, the results shown in Fig. 2 have been interpreted in terms of the Fermi level motion in relation to the demarcation levels of Fe, Cr, and Ni TA ions (Fig. 3), with TA gaining or losing electrons (charge transfer process) and, therefore, changing their valence states depending on the Fermi level position.

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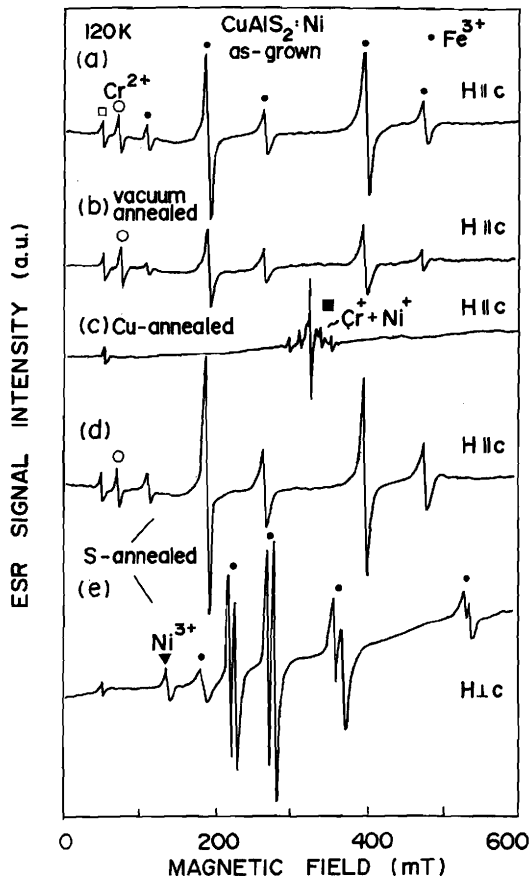


Fig. 2. ESR spectra of the CuAlS_2 crystals, doped with Ni, as well as subsequently annealed in various atmospheres (800°C, 60 h). ●, ○, ▼, ■ and □ marks correspond to the signals from Fe^{3+} , Cr^{2+} , Ni^{3+} , $\text{Cr}^{+} + \text{Ni}^{+}$ (two signals) ions and an unidentified impurity with a nearly isotropic $g=11.95$, respectively.

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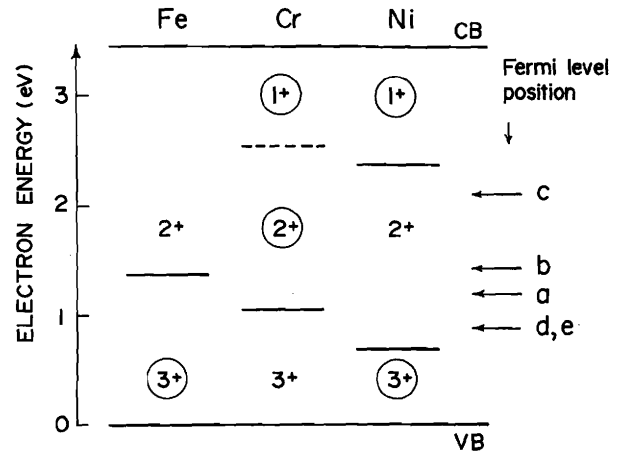


Fig. 3. A schematic energy level diagram of CuAlS_2 :Fe, Cr, Ni. The states detected by ESR are marked by ○. The position of the Fermi level in the band gap is indicated in the right part of the Fig. for: a— as-grown, b—vacuum annealed, c—Cu-annealed, and e, d—S-annealed samples. Note that the same indication is used in Fig. 2.

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