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Middle-infrared absorption and electron paramagnetic resonance of copper associates in zinc sulfide

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Résumé. — Après traitement thermique dans une atmosphère de soufre des cristaux de ZnS présentent, à basse température, un multiplet d'absorption dans l'infrarouge moyen (IRM) à $\bar{\nu} \approx 800 \text{ cm}^{-1}$. Une raie principale non polarisée est attribuée à la transition $(E, T_2)-^3T_1(F) \leftarrow A_1-^3T_1(F)$ des ions $\text{Cu}^{3+}(3d^8)$ sur des sites T_d dont la symétrie est réduite à C_{3v} par association avec un défaut X voisin. Par analogie, cinq satellites appartiennent aux complexes $[\text{Cu}^{3+}, X]$ de la symétrie C_s ; dans ce cas, le Cu est situé dans un environnement hexagonal. Par irradiation UV à $T \approx 4 \text{ K}$, la configuration de l'ion Cu est modifiée en d^9 en formant un complexe $[\text{Cu}^{2+}, X]$ qui, dans des expériences RPE est apparu comme le centre appelé Cu-« M » présenté dans un travail précédent (Holton *et al.*, 1969). Cet état du cristal est caractérisé par une absorption IRM à $\bar{\nu} = 868 \text{ cm}^{-1}$ et dans l'infrarouge proche par un spectre d'émission modifié.

Abstract. — After firing in sulphur atmosphere, ZnS crystals show at low temperature an absorption multiplet in the middle-infrared (MIR) region near $\bar{\nu} \approx 800 \text{ cm}^{-1}$. An unpolarized main line is assigned to the transition $(E, T_2)-^3T_1(F) \leftarrow A_1-^3T_1(F)$ of $\text{Cu}^{3+}(3d^8)$ ions on T_d lattice sites whose symmetry is reduced to C_{3v} by association with a neighbored defect X. Five polarized satellites refer likewise to associates $[\text{Cu}^{3+}, X]$ of symmetry C_s , the copper residing in a hexagonal environment in that case. Under UV irradiation at $T \approx 4 \text{ K}$, the configuration of the copper ion is changed into d^9 so that a complex $[\text{Cu}^{2+}, X]$ emerges which, in EPR experiments, figures as the Cu-« M »-centre known from an earlier study (Holton *et al.*, 1969). This state of the crystal is characterized by an additional MIR absorption at $\bar{\nu} \approx 868 \text{ cm}^{-1}$ and by a modified NIR emission spectrum.

1. Introduction.

Copper is one of the best known and most investigated activators for the photoluminescence of ZnS in the visible and infrared spectral regions. Not only is Cu present in various charge states [1, 2], it also forms various associates with intrinsic [3, 4] and extrinsic defects [5-7]. These features have been inferred from the dependence of the optical properties on the sample preparation, from polarization effects in the optical spectra [8-10], EPR measurements [11, 12] as well as ODMR investigations [13, 14].

A particularly important means for the determination of the microscopic symmetry of these centres is EPR at paramagnetic Cu^{2+} -associates. Holton *et al.* [11] alone found ten different species of copper associates in ZnS. Recently, a definite attribution of

the Cu-« H »-centre to certain luminescence bands has been obtained by means of ODMR [13]. Statements on the chemical nature of these centres are, however, difficult to achieve.

In this paper, an MIR absorption is reported which occurs at Cu-doped ZnS crystals and which is (based on symmetry considerations) ascribed to an already known EPR centre. Moreover, these findings are discussed in connection with new luminescence effects which have recently been found in this group [15, 16].

2. Experimental techniques.

The investigations have been carried out with ZnS crystals grown by four different methods. In case that copper doping was carried out here, the crystals were covered by a thin Cu layer and subsequently annealed for several hours, at 1 000 °C, in an evacuated quartz ampoule under sulphur atmosphere.

The near-infrared spectra show that all of the used crystals contained Cu impurities, even before the

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annealing. The presence of copper is a necessary but not a sufficient condition for an observation of the properties reported here. All crystals are of mixed cubic-hexagonal structure.

The initial IR-absorption measurements at these samples have been carried out with a vacuum grating spectrometer (type BB of CODERG, Paris). Later measurements have been made by means of a vacuum Fourier spectrometer (type IFS 113v of Bruker-Physik, Karlsruhe). This instrument allows measurements with a higher resolution ($\Delta\bar{\nu} = 0.5\text{-}1\text{ cm}^{-1}$) so that structures which had earlier barely been made out could now be resolved. The specimens are fastened to the cold finger of a continuous-flow cryostat (type CF 104 of Oxford Instr.) which allows measurements in the temperature region of 4-300 K.

In the EPR measurements, an X-band spectrometer (type 4504 of Varian) has been employed. The specimens are immersed in a helium-bath finger Dewar which is placed into a rectangular cavity kept at room temperature. The optical irradiation is made through the slotted resonator wall by means of a mercury high-pressure lamp (Osram HBO 200) and colour filters.

3. Experimental results.

All investigated crystals exhibit, more or less intensely, a narrow, structured absorption band near $\bar{\nu} = 800\text{ cm}^{-1}$ (cf. [17]). The crystals No. 3051 and 3092 show this effect after doping with Cu and subsequent annealing in sulphur atmosphere, whereas with crystals No. 3079 and 3103 this effect occurs even without additional doping by Cu, yet after the same thermal treatment as with the other two crystals. From emission measurements it is known, however, that crystals 3079 and 3103 also contain Cu as an impurity.

Crystal No. 3051 displays the IR absorption the strongest and most clearly (Fig. 1). At low tempera-

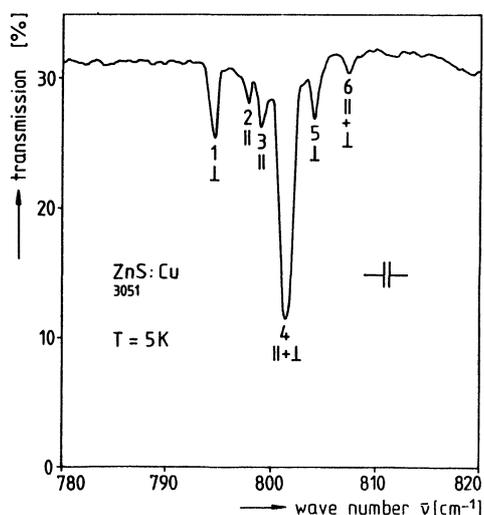


Fig. 1. — IR absorption of a Cu-doped and annealed ZnS crystal.

tures, the absorption consists of a central unpolarized line and five satellites, four of which prove to be polarized with a polarization degree $p > 80\%$. The main line ($\bar{\nu} \approx 802\text{ cm}^{-1}$) is observable up to 300 K; at this temperature it is, however, strongly broadened (half width $\Delta\bar{\nu} \approx 12\text{ cm}^{-1}$) and shifted by $\delta\bar{\nu} \approx 7\text{ cm}^{-1}$ towards smaller wave numbers. The satellite structures disappear for $T \gtrsim 100\text{ K}$.

A longer UV irradiation (near $\lambda \approx 360\text{ nm}$, i.e. $\bar{\nu} \approx 28\,000\text{ cm}^{-1}$) at low temperature produces at all crystals a further narrow-band unpolarized absorption at $\bar{\nu} = 868\text{ cm}^{-1}$ (Fig. 2) whose appearance, for crystals No. 3079 and 3103, is connected with the simultaneous quenching of the 800 cm^{-1} band. All crystals show in addition new broad luminescence bands at $\bar{\nu} = 4\,550\text{ cm}^{-1}$ and $\bar{\nu} = 6\,600\text{ cm}^{-1}$ which are enhanced after UV irradiation [15, 16].

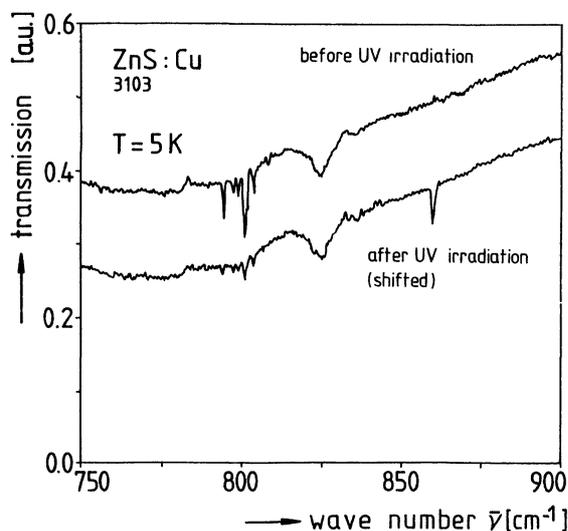


Fig. 2. — IR absorption spectrum of a Cu-doped ZnS crystal prior and after long UV irradiation, spectral resolution $\Delta\bar{\nu} \approx 0.5\text{ cm}^{-1}$.

An EPR spectrum typical for these crystals is given in figure 3 for the orientation $\mathbf{B} \parallel \mathbf{c}$. By comparing the g -factors and the hyperfine splittings with the results of Holton *et al.* [11], these signals can clearly be attributed to the so-called Cu-« M » and Cu-« H » centres found by these authors. With crystal No. 3051 whose 800 cm^{-1} band cannot be quenched, the resonance of the Cu-« M » centre appears only after very long and intensive UV irradiation. At the other crystals this resonance is enhanced by UV irradiation, as has been observed in reference 11. The resonance of the Cu-« H » centre is hardly visible with crystals cooled in the dark, appears however after very short blue or UV irradiation. Holton *et al.* [11] could no longer detect the resonances for temperatures above 2 K, whereas we still see them at 4.2 K. As the samples in the study [11] have, in contrast to our measurements, possibly not been in direct contact with a helium bath, this discrepancy may be due to a specimen temperature esteemed too low in Holton's experiment.

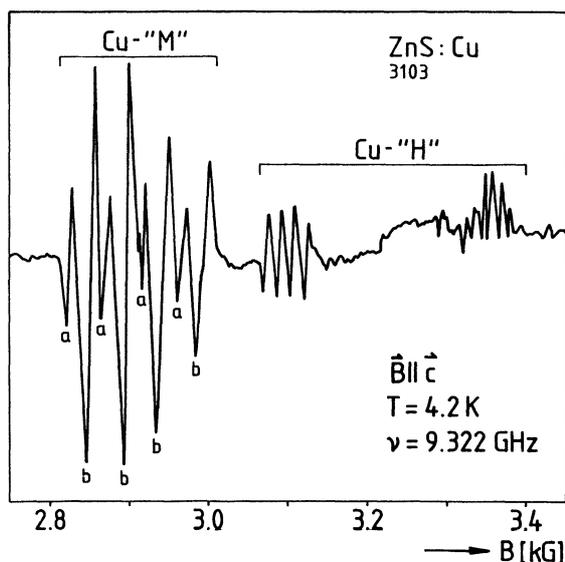


Fig. 3. — EPR spectrum of a Cu-doped ZnS crystal which displays the resonances of the so-called Cu-« H »- and Cu-« M »-centres.

In accordance with reference 11, we obtain for the Cu-« M » centre a g -factor $g_{\parallel} = 2.30$ and a hyperfine splitting $A(^{63,65}\text{Cu}) = 48 \times 10^{-3} \text{ cm}^{-1}$. These values relate to associates oriented in the direction of the c axis, as will be discussed in the next section. For other orientations, the EPR spectra are of such a confusing complexity that they cannot be evaluated any more.

4. Discussion.

The experimental results suggest strongly that the absorption around $\bar{\nu} = 800 \text{ cm}^{-1}$ is bound to the presence of Cu impurities in the investigated crystals. Emission and absorption measurements in the near infrared [18] demonstrate that in Cu-doped ZnS the Cu is found as $\text{Cu}_{\text{Zn}}^{2+}$ on a T_d lattice site. Due to the crystal field splitting of the 2D free ion term into a 2T_2 ground state and a 2E excitation state, this leads to characteristic bands in the NIR region around 7000 cm^{-1} . These bands are also observed with the crystals investigated here. A further splitting of the ground state by spin-orbit interaction into a lower Γ_7 state and an upper Γ_8 level (irreducible representations of the double group \bar{T}_d) is markedly reduced by dynamic Jahn-Teller interaction [19] versus the free-ion value $\zeta = 830 \text{ cm}^{-1}$ [20]. Hence, a transition $\Gamma_8(T_2) \leftarrow \Gamma_7(T_2)$ cannot explain the 800 cm^{-1} band.

The multiplicity and polarization behaviour of the absorption structure can, however, be interpreted by transitions between the $A_1-^3T_1(F)$ ground state and the components, as split in C_s symmetry, of the $E, T_2-^3T_1(F)$ level of a $3d^8$ configuration (see Fig. 4). Since Ni-doped ZnS crystals do not show this absorption, the $3d^8$ configuration of Ni^{2+} [21] can be excluded

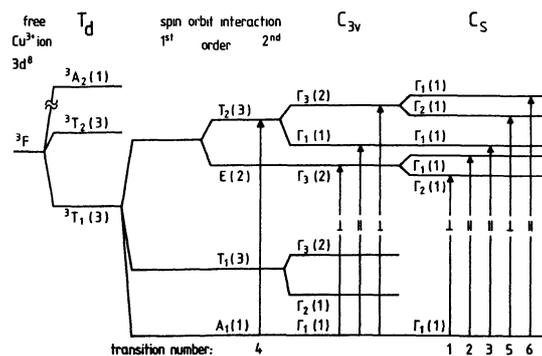


Fig. 4. — Level diagram of the spin-orbit and crystal field splittings of the $^3T_1(F)$ ground state of a $3d^8$ configuration in T_d symmetry. The degeneracies of the levels are given in brackets.

as a contingent source. Also with regard to the doping it is more logical to expect the $3d^8$ configuration of a Cu^{3+} ion, it would, however, have to be associated with an extrinsic ligand. This idea is supported by the fact that the effect occurs only after firing the sample which obviously favours the formation of associates. Alternative interpretations in terms of localized-mode vibrations of intrinsic defects (e.g. [22, 23]) or of internal electronic transitions involving shallow trap states (e.g. [24]) were considered but could be excluded with the help of semi-quantitative estimations.

From the one-electron spin-orbit coupling parameter $\zeta = 890 \text{ cm}^{-1}$, a many-electron parameter $\lambda = -\zeta/2 \approx -445 \text{ cm}^{-1}$ is obtained for the free Cu^{3+} ion (cf. e.g. [20]). With this λ -value, the $E, T_2-^3T_1(F)$ levels are predicted at $\frac{9}{2} |\lambda| \approx 2000 \text{ cm}^{-1}$ above the ground state. The apparent reduction of this separation to about 800 cm^{-1} in ZnS may be comprehensible by a combination of local distortions (cf. [25]) and covalency effects.

Since our crystals are all of cubic-hexagonal mixed structure, for a Cu^{3+} ion on a Zn site, the environment has either cubic (T_d) or trigonal (C_{3v}) symmetry. For a Cu ion on a C_{3v} lattice site, an associated partner on one of the four neighbouring lattice sites leads to a reduction to C_s symmetry unless the partner is situated in the direction of the c axis; otherwise the C_{3v} symmetry is maintained. The polarization selection rules determined by group theory for C_s symmetry (cf. Fig. 4) are here based on the following convention: \parallel means that the direction of the \mathbf{E} vector is contained in the C_s symmetry plane and \perp , that \mathbf{E} is perpendicular to this plane. The experiments reveal, however, a polarization dependence relative to the c axis, thus demonstrating that the influence of the ligands is dominated by the axial crystal field at the Cu^{3+} ion produced by the hexagonal lattice structure.

If the influence of the axial crystal field were zero or negligibly small (as, e.g. on cubic lattice sites or for $c/a = \sqrt{8/3}$), the polarization were determined by the spatial orientation of the C_s symmetry planes. In this

case, no polarization would be observable owing to the averaging effected by the random spatial distribution of the ligands of the copper.

About a quarter of the Cu^{3+} associates have to be oriented in the direction of the c axis and should display the three transitions within centres of C_{3v} symmetry depicted in the level scheme (Fig. 4). These are, however, not observed. In accordance with the above reasoning one could, however, assume that in this case the axial crystal field is enlarged by the associated ligand just to the extent that the three missing transitions meet with the lines No. 1, 3 and 6. This would also explain why line 6 is observed for both polarization directions.

The central unpolarized line 4 can be attributed to Cu^{3+} associates which comprise copper on cubic lattice sites, so that all of the associates have C_{3v} symmetry. Now only the influence of the ligands is effective. This interaction is, again in agreement with the preceding reasoning, considered as weak compared with the effect of an axial crystal field. Therefore, at these sites no splitting is observed but only a broadening of the absorption. The selection rules for the polarization are, of course, on these lattice sites determined by the directions of the four tetrahedral axes which can be assumed by the associates so that for this reasoning no polarization effects can be expected.

A Cu-« M » EPR signal of considerably higher intensity than that in the paper [11] suggests to advance a deviative interpretation of these resonances : the position and intensity of the two line groups « a » and « b » observed for $\mathbf{B} \parallel c$ exclude a $^{63}\text{Cu}/^{65}\text{Cu}$ isotopic effect. The Cu-« M » centres are Cu^{2+} associates with the partner on a neighboured lattice site, like the Cu-« H » centres. In contrast to these, the principal axis of the \mathbf{g} -tensor for line group « b » is, however, not determined by the direction of the pair axis but preferentially by the direction of the c axis. Therefore, we ascribe the weaker line group « a » to the associates oriented in the direction of the c axis, and the stronger group « b » to the associates oriented in the directions of the three other tetrahedral axes which form an angle of 70.5° with \mathbf{B} and the c axis for this orientation.

In this case, the influence of the ligands is noticeable by a minute tilting of the electrical field gradient from the c direction. Because of $g_{\perp} < g_{\parallel}$, the resonance of line group « b » is situated at somewhat higher fields. If the principal axis of the \mathbf{g} -tensor were defined by the pair axis as for the Cu-« H » centre, the resonance of line group « b » were as well positioned at much higher field strengths. When the magnetic field is tilted towards the direction $\mathbf{B} \perp c$, the whole line group is shifted to higher resonance fields, with the group « b » splitting into further lines, thereby complicating the whole spectrum.

The Cu-« M » centres thus show the same symmetry properties as the Cu^{3+} associates on hexagonal

lattice sites. We therefore assume that the Cu-« M » centres arise from these under UV irradiation :



This hypothesis is supported by the respective stimulation and quenching response of IR absorption and EPR signals. With crystal No. 3051, for which quenching of the MIR absorption is not possible, and where an EPR signal does not occur without irradiation, obviously only such a small portion of these centres change their charge state that the absorption spectrum is not affected.

Based on their appearance at all investigated crystals and on the corresponding stimulation/quenching behaviour, the mentioned 4 550 and 6 660 cm^{-1} emission bands are ascribed — less cogent though — to the $[\text{Cu}^{2+}, \text{X}]$ complex as well [15, 16].

The question arises why no resonance can be observed of the Cu-« M » centres on cubic lattice sites which we assume to be responsible for the central unpolarized line No 4 in the IR spectrum. A spectrum would have to be expected rather with an isotropic g -factor near 2, possibly comparable to the signals found in reference 4 for assumed associates $[\text{Me}_{\text{zn}}, \text{V}_s]^x$ of sulphur vacancies V_s with Cu^{2+} , Ag^{2+} or Au^{2+} ions (Me). For the absence of this resonance the same reasons can be responsible which also prevented the detection of the EPR of an isolated Cu^{2+} ion in ZnS up to now. As is known, the Cu^{2+} ion in ZnS is subject to a pronounced dynamic Jahn-Teller effect in the ground state [19, 26]. According to Clerjaud and Gelineau [27], this leads to an extremely strong coupling to the strain expected in ZnS crystals. Due to a strong dependence of the g -factor of the Γ_7 ground state on this strain, this would lead to such a great inhomogeneous broadening of the resonance that it would not be detectable any more. Hagston [28] ascribes the default of a resonance to a fast spin-lattice relaxation caused by the strong interaction of the copper with the ZnS lattice.

The existence of a Cu^{3+} charge state does not seem to be improbable with view to the fact that the considered crystals have all been fired in sulphur atmosphere, the Fermi level being situated very low in the band gap. Thus, Holton *et al.* [11] already suggest for their Cu-« R » centre an associate of a Cu^{3+} ion on a Zn site and a neighboured Zn vacancy : $[\text{Cu}_{\text{zn}}^{3+}, \text{V}_{\text{zn}}]^x$. We assume that in our centres the Cu is placed on a Zn site and the associated partner on a neighboured sulphur site : $\text{Cu}_{\text{zn}}\text{X}_s$. In the picture of a point-charge model the interaction with this partner is weak. We therefore suppose that in this case we have rather to do with a defect isoelectronic to sulphur, such as $(\text{V}_s^{2-})^x$, oxygen, selenium or tellurium. The mentioned impurities could have been present as a trace in the starting material, or may have entered the lattice during the annealing process.

In accordance with this idea is the inference of Godlewski *et al.* [13] that the so-called Cu-« H »

centre, which we also observed, is a Cu/donor pair with Cu on a Zn site and the donor D on a neighboured sulphur site : $\text{Cu}_{\text{Zn}}\text{D}_{\text{S}}$. In this case, the principal axis of the \mathbf{g} -tensor is determined by the four possible $\langle 111 \rangle$ directions in T_d symmetry, caused by the excess positive charge of the donors *versus* the sulphur ions.

Finally we want to offer a possible explanation for the additional absorption occurring at $\bar{\nu} = 868 \text{ cm}^{-1}$. Postulating that the dynamic Jahn-Teller effect assumed for isolated Cu^{2+} ions were not effective for the Cu-« M »-centre, the spin-orbit splitting of the 2T_2 ground state would equal $(3/2)\lambda$, where λ is the spin-orbit constant. With $\lambda = -830 \text{ cm}^{-1}$ for the free Cu^{2+} ion [20] and a presumed 30% reduction by covalency effects in ZnS (cf. [19, 29]), a splitting of

870 cm^{-1} can be estimated which is in nice agreement with the observed line position.

Parts of the results have been presented at the meeting of the Fachausschuß Halbleiterphysik, Deutsche Physikalische Gesellschaft, Münster 1982 [30].

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