20°K with $\sim$1- and 45-MeV electrons. It is not easy to correlate a macroscopic measurement with Watkins' measurements because there are so many different defect centers observed in the latter, even in the case of low-energy electron irradiation.

In FZ samples, the annealing of damage as measured by the reciprocal mobility is more rapid than in carrier concentration. The source causing this is unknown. It is possible that the dislocations in the samples play an important role for this phenomena, since the dislocations belong to one kind of the major imperfections in FZ crystals.

The production rate of the $A$ center which we obtain in pulled crystals irradiated by 45-MeV electrons at 80°K is comparable to that measured by Watkins[17] from spin resonance using the same energy electrons at room temperature. Ramdas and Fan[5] also have reported that the production rate of the 12-$\mu$ band ($A$ center) at 80°K is not significantly different from the production rate at 300°K in 4.5-MeV electron irradiations. These findings are different from the results[15,17] of 1-MeV electron irradiation, in which the production rate of the $A$ center at liquid-nitrogen temperature is about an order of magnitude less for pulled silicon irradiated at room temperature. Because of the close similarity of our data and the results of Hill,[14] Novak,[16] and Wertheim,[15] we conclude that a large number of defects produced by 45-MeV electrons at lower temperatures are similar to the defects found in low-energy electron irradiations. In other words, low-dose 45-MeV electron irradiations will not produce a larger number of high-order defects, such as clusters, as was originally anticipated; but instead, larger numbers of simple defects are produced.

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# Fine Structure of the Infrared Absorption and Emission Spectra of Cu$^{2+}$ in ZnS and CdS Crystals

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Near-infrared absorption and emission spectra of Cu$^{2+}$ as a substitutional impurity in ZnS and CdS crystals recorded at low temperatures are found to exhibit a pronounced fine structure. The optical transitions occur between energy levels which result from a splitting of the Cu$^{2+}$ ground state by a crystal field of tetrahedral symmetry and the spin-orbit interaction. A small contribution of lower symmetry—possibly produced by Jahn-Teller effect—and an interaction of the center with vibration modes of the host lattice account for the occurrence of numerous lines. Crystal field and spin-orbit parameters were calculated for Cu$^{2+}$ in ZnS and CdS crystals.

It is well known, that copper can act as an activator for luminescence in ZnS and CdS phosphors. Several emission bands in the visible[1] and near-infrared[2] spectral regions could be correlated to centers containing at least one Cu ion. Particularly detailed experiments have been performed to understand the chemical and electronic structure of the center leading to the emission bands near 1.5$\mu$ and to the corresponding absorption peaking at about 1.3$\mu$.[3–6] There is evidence by both chemical[5] and radioactive[6] methods that the incorporation of uncompensated copper on cation sites causes these infrared emission and absorption bands. As uncompensated copper forms a doubly charged ion with electron configuration $3d^9$ the system of electronic levels as well as the radiative transitions between them should be explainable by means of crystal field theory. This has been shown already for absorption in copper-

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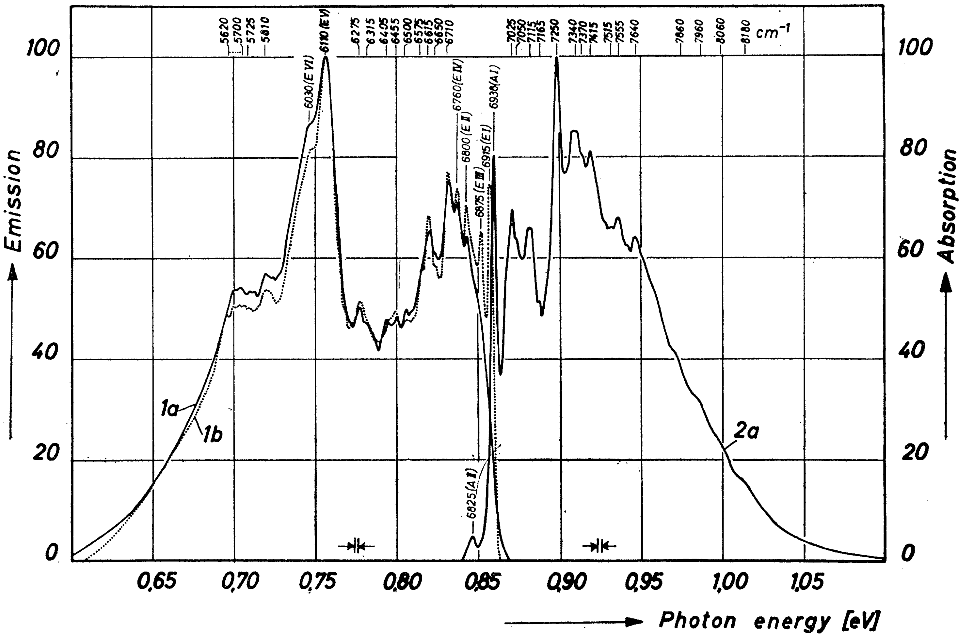

FIG. 1. Normalized emission (1) at 4.2°K and absorption (2) at 4.8°K of $Cu^{2+}$ in two different ZnS crystals (*a*,*b*).

activated ZnO and CdS crystals by other authors.[7–10] But there did not exist enough experimental evidence to include the more complicated infrared emission spectra into the same concept. Furthermore, no resolved absorption data for $Cu^{2+}$ in ZnS crystals were available until now. It is the aim of this paper to present the fine structure of both the infrared emission and absorption spectra of ZnS and CdS crystals measured at low temperatures and with relatively high resolution (17 $cm^{-1}$). Full information about the splitting of the $^2D$ term of $Cu^{2+}$ by crystal field and spin-orbit interaction in tetrahedral configuration can be drawn from the simultaneous knowledge of both types of spectra. In addition a vibronic structure has been detected and interpreted by using the known lattice vibration modes.

The vapor-grown ZnS crystals consist of a mixture of hexagonal and cubic structures; the CdS crystals are preferentially hexagonal. One of the ZnS crystals (No. 1) has been deliberately doped with copper, the other (No. 3) was subjected to neutron-induced radioactive activation ($Zn^{65} \rightarrow Cu^{65}$).[6] At the time of the measurement its copper content arising from this process was about $1.5 \times 10^{-5}$ (g Cu)/(g ZnS). Both of the CdS crystals have been activated by diffusing cathode-sputtered copper into the lattice at 730°C.

The absorption spectrum of the ZnS crystal No. 3 (Fig. 1, curve 2a) shows a pattern of highly resolved lines, but yet its shape is limited by the resolution of the apparatus. Assuming the sharp line on the low-energy side at 6938 $cm^{-1}$ (hereafter called *AI*) to be a zero phonon transition, we tried to identify the following peaks as phonon-coupled derivatives of this transition. At 7025 and 7115 $cm^{-1}$, respectively, one and two transverse acoustical phonons $TA_1 = 92$ $cm^{-1}$ of the hexagonal lattice are excited simultaneously with the electronic transition, whereas the subsidiary peaks at 7050 and 7165 $cm^{-1}$ seem to involve the phonon $TA_2 = 115$ $cm^{-1}$ of cubic ZnS.[11] The line at 7250 $cm^{-1}$ is explained as due to an interaction with an optical phonon[11,12] $TO = 312$ $cm^{-1}$ in this transition and is followed by a sequence of lines repeating the same pattern approximately. At wave numbers higher than the 7555-$cm^{-1}$ peak, occurring with participation of two TO phonons, the structure is less pronounced. The small peak at 6825 $cm^{-1}$ (*AII*)—a similar one has been detected in ZnO at 78°K[9]—can be ascribed to a second zero-phonon transition.

The emission spectrum of the same crystal under broad band excitation (1.4 eV$\leq h\nu \leq$4.0 eV) (Fig. 1, curve 1a) rises gradually in the 0.85 eV region, whereas the spectrum of ZnS No. 1 (Fig. 1, curve 1b) contains two lines here. The difference of the spectra may arise from the distinct physicochemical structure of the centers in the two crystals caused by different activation processes. The first of the lines in question, at 6915 $cm^{-1}$ (hereafter called *EI*), almost coincides with the dominant zero phonon line *AI* in absorption and is therefore considered to be due to the inverse transition. The small shift of 23 $cm^{-1}$ may be explained either by the limits of our experimental arrangements or by the

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fact that the compared transitions have been evaluated with two different crystals. Repeated measurements of both spectra with another crystal showed full coincidence of both lines. It might be mentioned that *EI* is the only line which depends at least partially superlinearly on the excitation intensity. The third peak at 6800 $\text{cm}^{-1}$ (*EII*) similarly is assumed to be connected with the minor zero-phonon line *AII* in absorption and is also somewhat shifted in energy. If one supposes *EI* and *EII* to be a doublet, the lines at 6875 $\text{cm}^{-1}$ (*EIII*) and 6760 $\text{cm}^{-1}$ (*EIV*) having a distance of 40 $\text{cm}^{-1}$ to *EI* and *EII*, respectively, indicate a second doublet structure. As no lattice vibration mode with an energy of 40 $\text{cm}^{-1}$ in ZnS is known, the assumption of a local mode due to the $Cu^{2+}$ center or of two further electronic transitions must be made. The following peaks which are in good accordance for the two crystals can be interpreted in terms of phonon interaction. For example, the coupling of one and two transverse acoustical modes with transition *EII* could account for the lines 6710 and 6615 $\text{cm}^{-1}$. The latter one can also be explained by a TO phonon coupled with transition *EI*.

The dominant lines at 6110 $\text{cm}^{-1}$ (*EV*) and 6030 $\text{cm}^{-1}$ (*EVI*) which correspond to no lines in the absorption spectrum and cannot be explained as phonon satellites are considered to be two more zero phonon lines. They are less narrow than the previous ones so that the second doublet which one might expect on their low-energy side separated from them by 115 $\text{cm}^{-1}$ is not resolved. The simultaneous excitation of one TO phonon explains the peaks at 5810 and 5725 $\text{cm}^{-1}$ as derivatives of *EV* and *EVI*, respectively. In addition the obscured second doublet becomes visible in the structured emission between 5700 and 5620 $\text{cm}^{-1}$ by this TO phonon interaction.

At least four pure electronic transitions are necessary to account for the structure in emission, two in absorption (Fig. 2). As an uncompensated $Cu^{2+}$ represents the infrared center, the origin of the inferred energy terms is to be explained by the splitting of the ground state of this $Cu^{2+}$ ion in crystal fields of tetrahedral symmetry. The splitting scheme of the $^2D$ level of $Cu^{2+}$ for hole transitions is included in Fig. 2 after Weakliem and McClure.[8] The splitting of the *G* levels could be caused by a superposition of a trigonal component probably by a Jahn-Teller effect. A second level near $E_{5/2}$, which possibly appears only after excitation of the center, could be indicated by the doublet *EIII*, *EIV*. But its origin is not yet explained. A value of the crystal field splitting 10 *Dq* has been derived approximately for ZnO[7–9] and CdS[10] from the absorption spectra of $Cu^{2+}$ in these substances. However, till now the spin-orbit coupling constant in tetrahedral coordination could only be estimated from electron spin resonance.[9] The spin-orbit splitting in octahedral coordination has been determined from the energetic difference of two absorption transitions.[7] The absorption method being scarcely practicable for tetrahedral sites,[8] a first optical determination of the spin-orbit splitting of the $^2T_2$ level becomes possible by the described emission measurements. By use of the relations indicated in Fig. 2 and of the positions of the dominant zero-phonon lines (6110, 6915 $\text{cm}^{-1}$), our data yield the following values for substitutional $Cu^{2+}$ ions on tetrahedral sites in ZnS:

$$Dq = 624\ \text{cm}^{-1}, \quad \zeta = 593\ \text{cm}^{-1}.$$

The corresponding absorption and emission spectra of $Cu^{2+}$ in cadmium sulfide have been recorded for comparison (Fig. 3). The absorption spectrum is

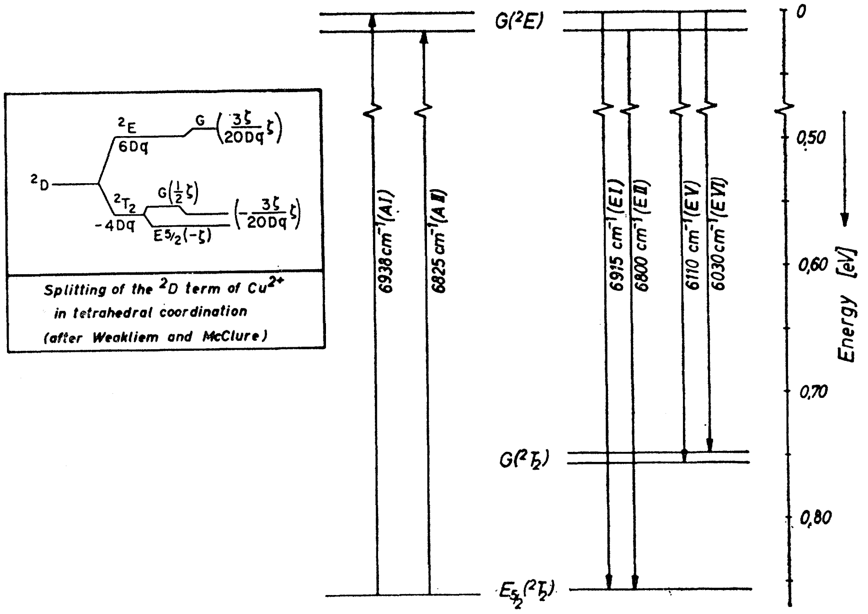

FIG. 2. Energy level diagram of a *d* hole in $Cu^{2+}$ from observed zero-phonon transition in ZnS.

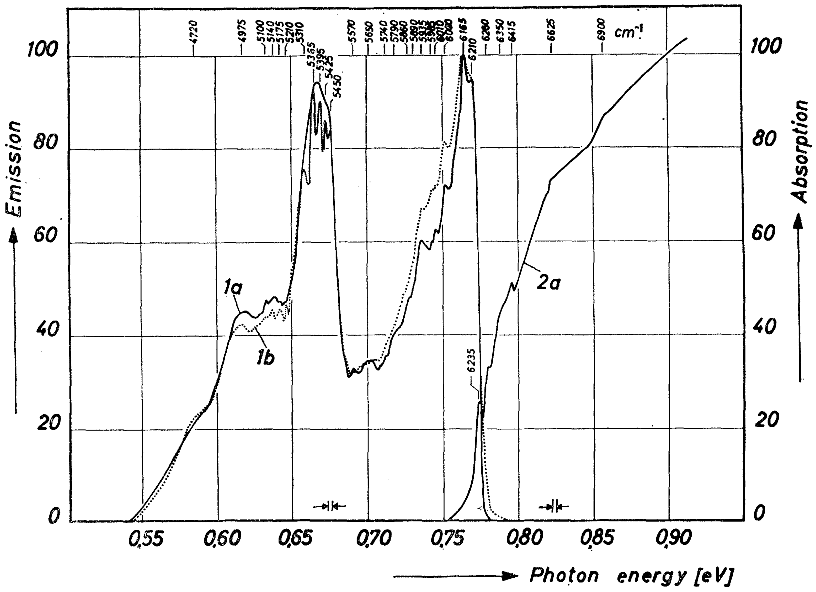

FIG. 3. Normalized emission (1) at 4.2°K and absorption (2) at 5.0°K of $Cu^{2+}$ in two different CdS crystals (*a*,*b*).

obscured in the relevant energy range by the flank of a broad band centered at about 0.94 eV. Hence, although the zero phonon line at 6235 $cm^{-1}$ is discernible, the phonon-coupled transitions are less pronounced here. The emission spectrum commences with the line at 6210 $cm^{-1}$ thus exhibiting a displacement of 25 $cm^{-1}$, very similar to the shift in ZnS:Cu (Fig. 1). In a distance of 45 $cm^{-1}$ it is followed by a line which presumably is the analog of peak *EIII* of ZnS:Cu but could also be explained by one of the recently determined TA phonons of CdS.[13] Among the various phonon-coupled lines the peak at 5935 $cm^{-1}$ involving a TO phonon is predominant. The reality of the structure in the 0.67-eV range, shown only by one of the two spectra, is doubtful because of the presence of water-vapor absorptions here. The 5450- to 5365-$cm^{-1}$ peaks might correspond to a splitting of the transition $G(^2E) \to G(^2T_2)$. This effect results from a trigonal component superimposed on the tetrahedral crystal field of CdS which in contrast to ZnS is a consequence of the crystal structure alone.[14] Its magnitude (about 25 $cm^{-1}$) seems to be reasonable in comparison with the splitting of the analogous levels in ZnO determined by absorption measurements.[7,8] The experiments on CdS:Cu, however, need a further extension to assure the reliability of the assignments. Using the stated zero-phonon lines 6210 and 5450 $cm^{-1}$ the parameters

$$Dq = 556\ \text{cm}^{-1} \quad \text{and} \quad \zeta = 565\ \text{cm}^{-1}$$

are calculated.

The absorption and emission processes treated here are restricted to an isolated center and do not imply electron transitions between its levels and the energy bands of the crystal. This problem is related to charge transfer changing[15] the ionic state of $Cu^{2+}$ to $Cu^{+}$ and possibly to $Cu^{3+}$, too.[16] Though several attempts have been made to state the energetic position of the $Cu^{2+}$ and $Cu^{+}$ within the band scheme of crystal phosphors,[4] there are still some open questions. However, knowing the electronic structure of the center itself one might be able to perform some specific experiments involving quenching and stimulation of the visible luminescence or photoconductivity to solve the mentioned problem.

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