Additional weaker structure at lower magnetic fields, where $r_c > \delta$, has been ascribed to nonlocal effects, possibly subharmonics of Azbel-Kaner resonance. Such nonlocal effects cannot be explained by the classical theory. No attempt has been made in this paper to derive a more complete theory valid in the region where $r_c \gtrsim \delta$. Such a theory would be extremely useful. The results of this experiment, however, indicate that the classical skin-effect theory is still a good approximation when $r_c/\delta \lesssim 1$, at least for relatively low values of $\omega\tau$.

Because the importance of the nonlocal effects increase as the carrier concentration is increased, measurements of the microwave cyclotron absorption in PbSe in a series of samples covering a wide range of carrier densities would be very useful in determining how the nonlocal effects modify the magnetoabsorption from that expected from the classical skin-effect theory. Such experiments would also allow the variation of the effective mass with carrier concentration and the mass at the band edge to be determined with a potentially greater degree of accuracy than has previously been possible with other methods.

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Fine Structure of Infrared Absorption Spectra of an Electroluminescent ZnS(CuCl) Crystal during Emission*

Aldo Cingolani† and Andrea Levialdi†
Istituto di Fisica, Universita di Messina, Messina, Italy

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In an electroluminescent ZnS(Cucl) polytype crystal, we studied the variation of the absorption spectrum in the near infrared, produced by the electric field responsible for electroluminescence. A highly frequency-sensitive detection method is used. When the electric field reaches the electroluminescence threshold, we observe an absorption in the infrared consisting of eight well-defined bands at 1.27, 1.21, 1.13, 1.06, 0.99, 0.93, and 0.87 eV. The temperature, phase, and frequency dependence of $\Delta I/I_0$ (I_0 is the intensity of the radiation after reflection or transmission of the nonexcited crystal) is analyzed and discussed, taking into acount the lifetime of the Cu^{++} center. Four of the eight peaks are quite broad, and can be attributed to transitions between the valence band and localized levels, and four are sharp and are attributed to internal electronic transitions assisted by phonons.

I. INTRODUCTION

A FUNDAMENTAL problem of electroluminescence (EL) is the nature of the impurity responsible for emission. In particular it must yet be shown which state of ionization of the impurity is present in equilibrium and during the excitation due to electric field.

A center in ZnS(CuCl) that has been very widely studied, in both electro- and photoluminescent phosphors, is copper. Here the presence of two intense emission bands, one blue and the other green, has suggested the presence of two different emission levels localized at different energies from the conduction band.

Birman[1] suggested a theoretical model that analyzed the eigenstates of the copper center in ZnS subject to a cubic crystalline field. Because of the effect of the latter, the electrons in the $3d^{10}$ configuration of Cu$^+$ are split into two groups: $d(T_2)$ and $d(E)$, with six T_2 levels and four E levels, separated by an energy equal to 10 Dq ($Dq=0.073$ eV).

The Cu^{++} center after ionization can have either configuration $(T_2)^5(E)^4$ or $(T_2)^6(E)^3$ until it relaxes to the ground state. After ionization the energy gap T_2-E is increased and both levels have moved away from the valence band because of lattice relaxation.

Schulz[2] and Broser's[3] model is a more phenomenological re-elaboration of Birman's theoretical concepts, in which only the splitting due to the cubic crystal field and lattice relaxation displacements are retained from the Birman model. Schulz's model (Fig. 1) shows the Cu$^+$ having 2 levels in the forbidden band. Four cases may arise: (1) both levels are occupied by electrons: Z^{2-}; (2) only the lower level is occupied: Z^-; (3) only the upper level is occupied: $(Z^-)^*$; (4) neither level is occupied: Z^0. Obviously, the model deals only with those electrons that may be removed by photons

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† Present address: Istituto di Fisica-Università di Bari, Bari, Italy.

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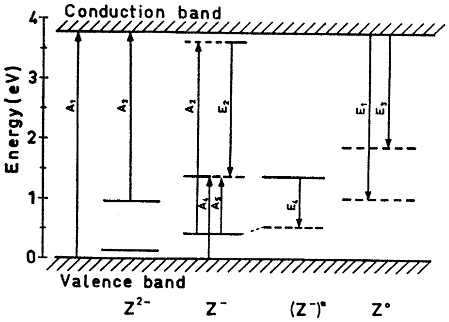

FIG. 1. Schulz's model.

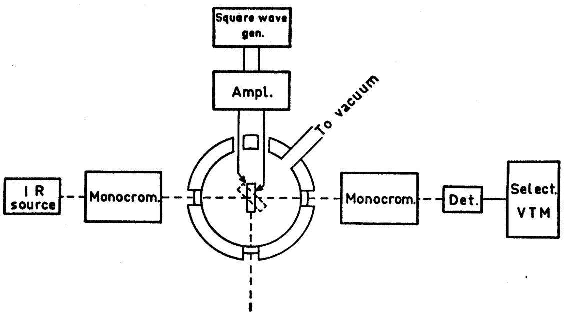

FIG. 2. Experimental apparatus (Select V. T. M. means selective voltmeter).

or electric field excitation. The lattice relaxation due to the Z^{2-} center after ionization can be deduced from Fig. 1. Its value is 0.4 eV. In this model the absorption A_4, which represents the transition from the valence band to the centers, is $h\nu = 1.3$ eV, whereas A_5 corresponds to the energy gap $T_2 - E$, and has the value $h\nu \simeq 0.9$ eV. Other authors[4–6] have assumed that Cu centers exist in several different charge states during the various luminescent processes, and they provide various interpretations of the internal transition of Cu^{++}. Broser[4] *et al.* account for the fine structure of the infrared (I.R.) absorption and emission in ZnS(Cu) and CdS(Cu) on the basis of electron-phonon interactions. Others[5,6] have interpreted their measurements of the I.R. absorption in ZnO(Cu) taking into account the splitting due to spin-orbit coupling and the trigonal symmetry C_{3v} of electronic levels $d(T_2)$ and $d(E)$ of the Cu^{++} ion.

The purpose of the present work is to study the infrared absorption that occurs while the EL crystal emits light. In ZnS the transitions in the near infrared involve states within the impurity center and states of the valence band. A sensitive technique is needed in order to detect transitions of low probability. The technique used is that of exciting the crystal with a square-pulsed electric field and measuring the absorption while the electric field is on.

This is done by means of a frequency-sensitive detector synchronized at the same frequency as the electric field. In Sec. II we describe the experimental technique and details concerning the samples used. In Sec. III we present the results obtained. In Sec. IV we give a discussion of the results and correlate them to the state of ionization of the impurity center.

II. EXPERIMENTAL

Reflection and transmission measurements were carried out on a polytype (wurtzite and blende) ZnS[CuCl) crystal, $\simeq 1$ mm thick, mounted in a "sandwich" between the layer of mica and two semitransparent, conductive glass plates. These measurements were made in the near infrared region (0.75 to 2 μ) in a temperature interval varying from -185–20°C, with the crystal under excitation by a rectangular-pulsed electric field (frequency from 20–2000 Hz). Since our crystal is mounted intrinsically (i.e., no current passes through it), EL emission occurs only during the field transients. Such emissions due to transients had an extinction time of 10^{-4} sec., i.e. at least one order of magnitude shorter than the time necessary to apply the electric field at the frequencies employed.

Our measuring technique was simple modulation of a type appropriate for revealing relative absorption variations $\Delta I/I_0$ of 10^{-5}–10^{-6} with phase-sensitive detection, and 10^{-4}–10^{-5} with narrow-band amplification.

The measurement of I_0 was carried out previously by measuring reflectivity or transmission of the nonexcited crystal.

The measurements of ΔI were carried out at different frequencies and at different amplitudes of the electric field, particularly at values higher than those corresponding to EL emission from transients. The signal ΔI is a measure of the variation in crystal absorption in the two extreme conditions for which the external electric field, of a rectangular shape, is respectively maximal and zero.

The general scheme of the experimental technique is shown in Fig. 2.

The infrared source and the monochromator used to provide the incident radiation are Bausch and Lomb Model 33-86-25-03. The infrared source is a tungsten filament lamp, fed by 108 W at 6 V. The monochromaticity $\Delta\lambda/\lambda = 0.01$. Reflected or transmitted radiation was analyzed using a Hilger and Watts flint prism, model *D* 285, to separate the wavelengths of the reflected or transmitted infrared from any possible infrared emission. Radiation detection was carried out using a Kodak Ektron PbS Type N-C 25 (10×10 mm) capacitively coupled with a selective voltmeter synchronized with the electric field frequencies.

The voltmeter is a Bruel and Kjaer type 2107, re-

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sponding in a frequency range of from 2 Hz to 40 kHz. In our working conditions, the noise was 18 dB below the minimum signal. The electric field for excitation was provided by a Hewlett-Packard square-impulse generator, model 211 A, followed by a voltage amplifier.

III. RESULTS

A. Selective Absorption of the Excited Center

When the value of the electric field is smaller than the value required to obtain the EL emission, we do not observe any absorption due to the field. When the value of the field is above the threshold for EL we observe an absorption spectrum in the region of the near infrared.

This spectrum is shown in Fig. 3. It presents 8 well-defined bands: four of these correspond to $h\nu = 1.27$ eV, 1.21 eV, 1.13 eV and 1.06 eV, respectively, and are rather wide, recalling the absorption band due to transitions between a continuum and a localized level; the remaining four are much narrower and seen to characterize the absorption lines due to internal transitions in the luminescent center.

The absorption spectrum shown in Fig. 3 is associated with the EL excited state of the crystal and in fact appears only when the excitation threshold is overcome, that is, when the crystal emits EL light.

The relative change in absorption $\Delta I/I$ was measured as a function of λ using measurements of both the reflection and the transmission intensity of a radiation beam, with the c axis of the crystal parallel to the electric field. In both cases we obtained the same position of the peaks. Under identical conditions of sensitivity and within the same wavelength range used for measuring selective absorption, no infrared emission, and no emission due to the electric field alone nor stimulated by the absorbed infrared, was found.

B. Relationship between Absorption and Temperature

Figure 4 shows the amplitude variation of three absorption peaks as a function of temperature. We have reported only results concerning three of the peaks, having assured ourselves that the remaining five behave the same way. From the figure one notes that there are two temperatures (−50°C and −95°C) for which $\Delta I/I_0$ is maximum even though dependence on λ remains unvaried. One should recall that the EL spectrum of our crystal at liquid-nitrogen temperature shows an intense blue band and a weak green one, whereas at room temperature one has a weak blue band and an intense green one.

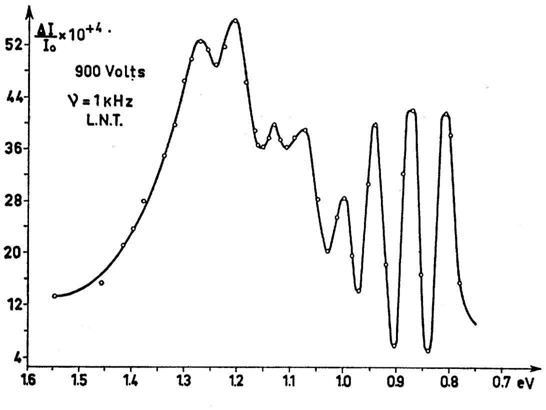

FIG. 3. Infrared absorption spectrum of the crystal during emission at liquid-nitrogen temperature.

C. Relationship between Absorption and Voltage

Figure 5 shows the dependence of absorption (particularly at its maximum) on applied external voltage. Only five of the eight peaks are illustrated, since the remaining three appear superimposed. In the voltage range to which the crystal was submitted [from 400 V (excitation threshold) to 900 V], the absorption increases linearly with the voltage. Within the limits of our measurement precision the positions of the absorption peaks remain invarient. The slope of the line corresponding to the variation of the absorption peak at $h\nu = 1.21$ eV diverges from the other seven, which are parallel to one another.

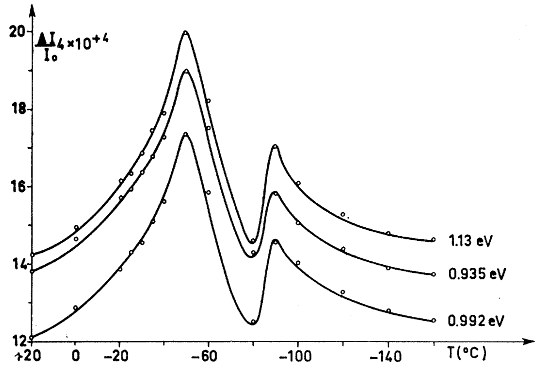

FIG. 4. Variation of the absorption peaks as function of temperature.

D. Relationship between Absorption and Electric Field Frequency

Variation in electric field frequency causes change in the height of all eight absorption peaks, although their position in the spectrum remains unchanged. The highest peaks are found as 1 kHz. At this frequency, the absorption, modulated by the field, is in phase with the excitation field. Absorption is frequency-dependent. The minimum corresponds to $\simeq$400 Hz. Below and above this frequency, the absorption increases. As said before, for frequencies higher than 1kHz the two periodic functions, excitation and absorption, are in phase: as the frequency decreases, the phase shift

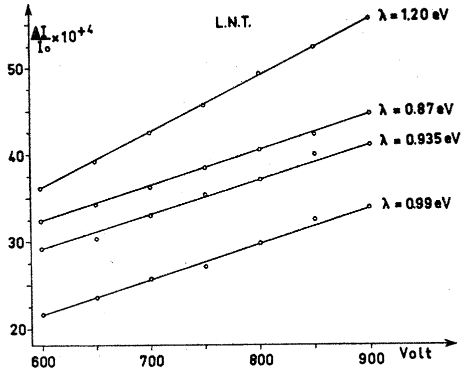

Fig. 5. Variation of the absorption as function of external applied voltage (L.N.T. = liquid nitrogen temperature).

increases continuously until phase opposition is reached at 30 Hz.

IV. DISCUSSION

Since the three peaks having energy values $h\nu = 0.93$ 0.87 and 0.80 eV coincide with the differences between the ^2E and the $^2T_2$ level, and are sharp, it is reasonable to assume that they correspond to internal transitions in the Cu^{++} center. Experimentally, one finds that they are separated by $\simeq 0.07$ eV. This separation does not coincide with the splitting of the ^2E state. Other authors[4,6,7] have measured and calculated values of from 0.005–0.013 eV for the splitting of the ^2E (doublet) and $^2T_2$ (triplet) levels due to spinorbit coupling and the trigonal symmetry C_{3v}. Furthermore, except for the shift due to lattice relaxation of transition $Z^- \rightarrow (Z^-)^*$ ($\simeq 0.1$ eV), the absorption for $h\nu = 0.93$, 0.87 and 0.80 eV may be correlated with the infrared emission observed for $h\nu = 0.84$, 0.75, and 0.70 eV.[8] The infrared emissions have been interpreted[2] from the viewpoint of the electron-phonon interaction, i.e., as fundamental infrared emission plus others assisted by LO phonons of 360 cm^{-1} (0.045 eV). It is therefore reasonable to ascribe the four "sharp" peaks with energy values 0.80, 0.87, 0.93, and 0.99 eV to internal transitions in the Cu^{++}, assisted by phonons (taking the peak at 0.80 eV to be the zero-phonon transition), rather than to the fine structure of levels $d(E)$ and $d(T_2)$. It is interesting to note that the following values are found in literature for the zero-phonon transitions[9]: 0.77 K (calculated) and 0.84 eV (measured).

It is beyond the scope of the present work to determine whether the energy of the phonons that assist our absorptions is analogous to that of those that assist the emissions. The question is a complex one for the following reasons: the measurements of $\Delta I/I_0$ are carried out during visible electroluminescent emission, and what is more, the modulation effect of the infrared absorption occurs precisely in the region of high electric field (the barrier), where $V \geq 10^5$ V/cm, and the currents create "friction" with the lattice (hot electrons). Therefore, the presence of these very high internal electric fields alters the vibrational state of the lattice. We are thus dealing with a rather complicated effect, i.e., optical absorption assisted by lattice phonons in the presence of a high, oscillating electric field, with the latter altering not only the vibrational state of the lattice but also the electron-phonon coupling which one finds in nonelectroluminescent ZnS.[10]

As regards the fine structure between 1.35 and 1 eV, since the absorption peaks form broad bands, one may reasonably suppose that they are due to transitions from the energy levels of the valence band to the emission centers. In principle, for this energy range one may have transitions from the valence band to the state Z^- (Cu^{++}) and to the state Z^0 (Cu^{3+}). One may exclude the possibility of absorption by this latter center for the following reasons:

(1) The variation of $\Delta I/I_0$ with T (Fig. 4) indicates that we are dealing with absorption by the Cu^{++} centers, of which one finds the maximum concentration at $\simeq -50$°C (as may be observed from measurements of E_2 emission), and consequently a maximum $\Delta I/I_0$. Below $\simeq -50$°C, the concentration of Z^- centers decreases and that of Z^0 centers increases, so that the E_1 (blue) emission starts prevailing, giving rise to the transition $Z^0 \rightarrow Z^-$. Because of this transition, there is an optimum temperature (second peak in Fig. 4) at which the concentration of Cu^{++} centers will start rising again: in fact the centers ionized by the electric field decrease as those produced by transition $Z^0 \rightarrow Z^-$ increase. Below this temperature ($\simeq -95$°C), the number of absorption centers again decreases, since they are only present because of the $Z^0 \rightarrow Z^-$ transition.

(2) The mean lifetime of the Z^0 centers is extremely short[2] so that, since the modulation frequencies at which we are measuring are relatively low, one may exclude absorption on the part of these centers (unless the center absorbs during electric excitation transients, in which case ΔI would not be revealed by our PbS detector, which loses its sensitivity at $\simeq 10^{-4}$ sec).

(3) Lastly, if one measures the phase difference between ΔI and the externally applied electric field, one finds that they are in phase at frequencies $\simeq 1$ kHz for all energy values represented in Fig. 3. Furthermore, at frequencies $\simeq$ 1 kHz one has maximum $\Delta I/I_0$. All the foregoing points to the conclusion that it is the Cu^{++} centers that absorb infrared radiation; in fact, for these centers one finds a mean lifetime of 10^{-3} sec.[11]

In interpreting the transitions corresponding to the energy peaks $h\nu = 1.27$, 1.21, 1.13 and 1.06 eV, one must

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keep the following in mind: the ZnS(CuCl) crystals, on which we carried out our measurements, are a polytype of a mixed hexagonal-cubic structure, so that, as one finds from measurements of green electroluminescent emission[12] two emitting Z^- states are present, one for each structure, at different energies from the valence band. Furthermore, taking the valence band to be made up of states separated from one another by 0.05 and 0.08 eV, the transitions arising from the two upper levels of the valence band to the Cu^{++} center are clearly visible, and precisely localized, whereas the transition from the continuum to the center does not appear: in fact, although our method allows us to detect $\Delta I/I_0 \simeq 10^{-5}$, when absorption of I_0 is too great, $\Delta I/I_0$ is no longer measurable, even though ΔI is of the same order of magnitude as in the other measurements. This is the case of transitions from the continuum to the Cu^{++} center. From the foregoing one may associate the four broad peaks with transitions from the two levels at the top of the valence band, to the $d(E)$ levels of the two Cu^{++} centers, one present in the cubic and the other in the hexagonal phase. This is reasonable if one takes into account the separation observed between the first pair of peaks and the second pair ($\simeq$0.13 eV), which corresponds to the energy difference one finds between the green emission of the Cu^{++} center in the hexagonal phase and that in the cubic phase ($\simeq$0.125 eV).[12]

Our experimental findings show that the position of the absorption peaks does not vary with applied voltage, whereas the height of the peaks varies linearly with the latter. The possible effect of the field on internal transitions within the center (Stark effect) cannot be detected on our instruments. There is, however, no infrared absorption spectrum shift as a function of applied voltage. The increase in peak height, with no spectrum shift, might show that the number of crystal regions in which the local field has acquired sufficient intensity to excite the centers increases, and in each of these regions the field reaches a value which, for some reason, cannot be surpassed. This may be explained as follows: The applied voltage is such as to increase the barrier field; tunneling increases the number of carriers that travel through the barrier, diminishing its resistance and consequently its potential difference. This mechanism prevents the field from growing beyond a certain value.

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Hall Effect in CoO, NiO, and α-Fe_2O_3

H. J. VAN DAAL AND A. J. BOSMAN
Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands

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The Hall coefficient R_H and resistivity ρ have been measured on ceramic samples of p-type CoO and NiO between 200 and 1500°K and of n-type α-Fe_2O_3 between 960 and 1500°K. Results obtained on single-crystal p-type NiO are also reported. Seebeck-effect data are considered in the discussion of the results. For the paramagnetic phase of NiO and α-Fe_2O_3, the behavior of R_H deviates drastically from that found in the case of a normal-band semiconductor. The sign of R_H is opposite to that normally expected. The corresponding Seebeck effect has the normal sign. R_H remains inversely proportional to the charge-carrier concentration. Furthermore, the Hall mobility ($\mu_H = |R_H|/\rho$) has a value which is smaller than that for the corresponding drift mobility (μ_D). The difference amounts to two orders of magnitude in the case of NiO and to about a factor of 4 in the case of α-Fe_2O_3. Below the Néel temperature, R_H has the normal sign. The anomalous behavior of the Hall effect in the cases of NiO and α-Fe_2O_3 is thought to be due to an interaction between the charge carriers and the magnetization induced in the material by the applied magnetic field. In the case of CoO the behavior of R_H does not seem to be influenced appreciably by the magnetic transition at the Néel temperature. The value of μ_H at high temperatures in the paramagnetic phase is about a factor of 4 lower than that of μ_D. A discussion of the Hall-effect data with regard to the mechanism of electrical conduction in the materials under consideration is also presented.

I. INTRODUCTION

THE mechanism of electrical conduction in transition-metal oxides such as CoO, NiO, and α-Fe_2O_3 has for long been the subject of extensive investigations. According to Verwey and de Boer[1,2] the occurrence of electrical conduction for example in NiO is associated with the presence of Ni ions with different valency at normal lattice sites. This situation can be easily obtained by employing the method of "controlled valency".[3] The introduction of Li into NiO, for instance, results in the formation of (Li^+-Ni^{3+}) acceptor centers.

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