ditional broadening at higher temperatures must be taken into account.

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Effect of a Vacancy on the Jahn-Teller-Distorted Γ_4^- Excited States in KI:Sn^{2+} as Observed in Polarized Luminescence*

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Four emission bands related to the A and C excited states, $A_{T\Pi}$, $A_{T\Sigma}$, $C_{T\Sigma}$, and $C_{T\Pi}$, have been observed in KI:Sn^{2+} at 4.2°K, and the degree of polarization has been studied. The results indicate that the Γ_4^- ($^3T_{1u}$ and $^1T_{1u}$) excited states are tetragonally distorted by a strong Jahn-Teller effect and are also perturbed by a charge-compensating vacancy located in the nearest-neighbor position.

The $^3T_{1u}$ and $^1T_{1u}$ ($a_{1g}t_{1u}$) excited states of Tl$^+$-type centers in alkali halides are characterized by a strong Jahn-Teller effect (JTE).[1] Most investigators[1-8] believe that the polarized luminescence from the monovalent impurity-ion (Tl$^+$, In$^+$, and Ga$^+$) centers is caused by the JTE. However, many of them[8-12] still believe that the polarized luminescence from the divalent impurity-ion (Pb^{2+} and Sn^{2+}) centers is mainly due to a charge-compensating vacancy; they have considered the effect of the vacancy to be more important than the JTE. The analysis of the absorption-band shape has, however, shown that the JTE in the divalent impurity-ion centers is much stronger than in the monovalent ones.[13-15] In this Letter we report the polarization spectra of luminescence from the Γ_4^-($^3T_{1u}$ and $^1T_{1u}$) excited states in KI:Sn^{2+} at 4.2°K, which clearly demonstrate a strong JTE and an effect due to the vacancy that is weaker than the JTE. Luminescence was observed with an EMI 9558QB photomultiplier after being dispersed by a single-grating monochromator; excitation was accomplished with a xenon lamp in combination with a double-prism monochromator. Sample crystals were always quenched from 650°C onto an aluminum foil at room temperature.

Excitation in the A absorption band produces two emission bands, $A_{T\Pi}$ (2.23 eV) and $A_{T\Sigma}$ (2.40 eV); the ratio of intensities between them depends on the photon energy of the exciting light.[1] The degree of polarization for $A_{T\Pi}$ or $A_{T\Sigma}$,

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}),$$

depends on the direction of polarization and the photon energy of the exciting light, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of $A_{T\Pi}$ or $A_{T\Sigma}$ polarized parallel and perpendicular to the direction of polarization of the exciting light, respectively. We used the exciting light incident upon the (100) plane perpendicularly so that the direction of polarization is specified by the azimuthal angle α in the (100) plane. The degrees of polarization $P(\alpha;A_{T\Pi})$ and $P(\alpha;A_{T\Sigma})$ as functions of α have a maximum at $\alpha=0°$ and 90° (in the [001] and [010] directions) and become zero at $\alpha=\pm45°$ (in the [011] and [0$\bar{1}$1] directions), irrespective of the photon energy of exciting light, $\hbar\omega$. In Fig. 1 are shown the degrees of polarization $P(\hbar\omega;A_{T\Pi})$ and $P(\hbar\omega;A_{T\Sigma})$ as functions of $\hbar\omega$ (the polarization spectra) at $\alpha=0°$ for $A_{T\Pi}$ and $A_{T\Sigma}$. Characteristic features are as follows: (A1) $P(\hbar\omega;A_{T\Pi})$ is

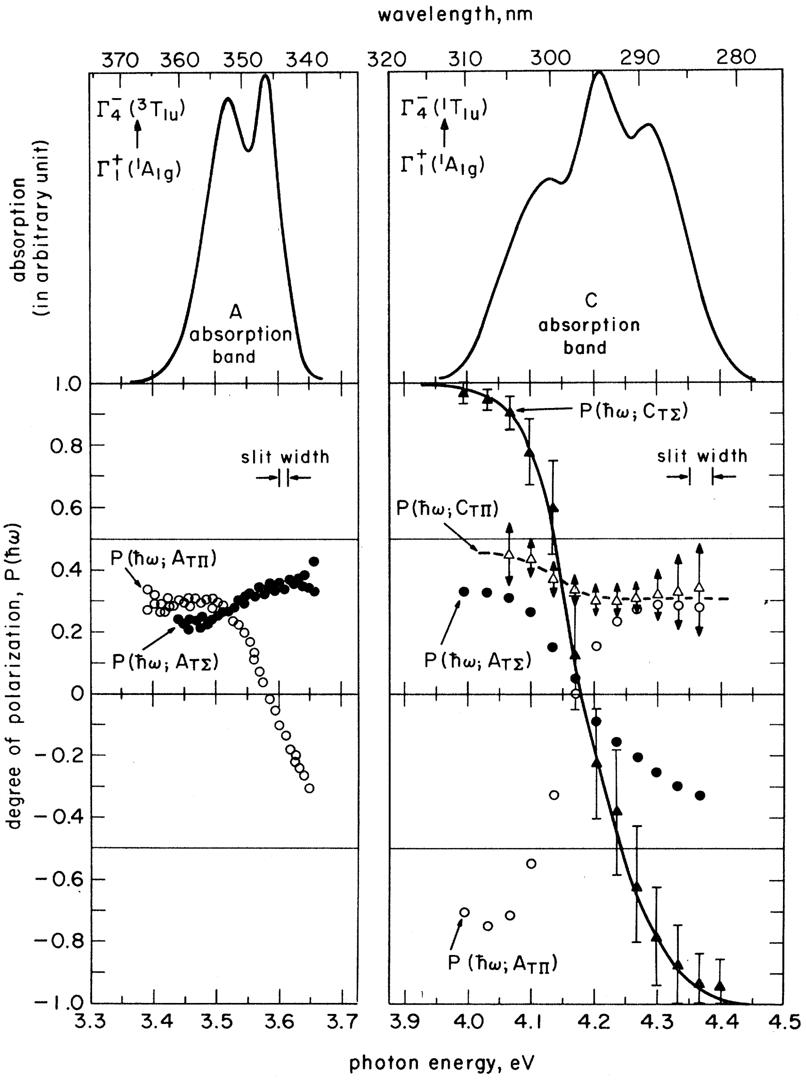


FIG. 1. Polarization spectra for the $A_{T\Pi}$, $A_{T\Sigma}$, $C_{T\Sigma}$, and $C_{T\Pi}$ emission bands in the A and C absorption region at 4.2°K. Exciting light was incident upon the (100) plane perpendicularly and was polarized in the [001] direction. Emitted light was observed from the [010] direction. Errors in $P(\hbar\omega; C_{T\Sigma})$ and $P(\hbar\omega; C_{T\Pi})$ are mainly caused by the fact that $C_{T\Sigma}$ and $C_{T\Pi}$ not only overlap each other but also overlap with the emission bands from the B excited states.

much less than unity even in the low-energy tail of the A band. ($A2$) $P(\hbar\omega; A_{T\Pi})$ decreases and then becomes negative as $\hbar\omega$ increases. The largest negative value is more than −0.3. ($A3$) $P(\hbar\omega; A_{T\Sigma})$ is smaller than $P(\hbar\omega; A_{T\Pi})$ in the low-energy tail. ($A4$) $P(\hbar\omega; A_{T\Sigma})$ increases with $\hbar\omega$, crosses $P(\hbar\omega; A_{T\Pi})$ near the peak of the A band, and becomes larger than 0.3 in the high-energy tail.

Emission spectra produced by excitation in the C absorption band are very complicated because of energy transfer from the C excited state to the B and A excited states. The two high-energy emission bands, $C_{T\Sigma}$ (3.33 eV) and $C_{T\Pi}$ (3.45 eV), are related to the C excited state because $C_{T\Sigma}$ and $C_{T\Pi}$ are not produced by excitation in the B or A bands. Excitation in the low-energy tail of the C band mainly produces $C_{T\Sigma}$, while excitation in the high-energy tail produces both $C_{T\Sigma}$ and $C_{T\Pi}$. Both $P(\alpha; C_{T\Sigma})$ and $P(\alpha; C_{T\Pi})$ also have a maximum at $\alpha = 0°$ and 90° and become zero at $\alpha = \pm 45°$, irrespective of $\hbar\omega$. In Fig. 1 are also shown $P(\hbar\omega; C_{T\Sigma})$ and $P(\hbar\omega; C_{T\Pi})$ at $\alpha = 0°$. There are four characteristic features: ($C1$) $P(\hbar\omega; C_{T\Sigma})$ is nearly unity in the low-energy tail of the C band. ($C2$) $P(\hbar\omega; C_{T\Sigma})$ decreases as $\hbar\omega$ increases and becomes nearly −1 in the high-energy tail. ($C3$) $P(\hbar\omega; C_{T\Pi})$ is much less than unity even in the low-energy tail. ($C4$) $P(\hbar\omega; C_{T\Pi})$ seems to decrease as $\hbar\omega$ increases, though it does not become negative even in the high-energy tail.

Excitation in the C absorption band also produces polarized $A_{T\Pi}$ and $A_{T\Sigma}$ emission bands. The following are the characteristic features: ($AC1$) $P(\hbar\omega;A_{T\Pi})$ has a rather large negative value, -0.7, in the low-energy tail of the C band. ($AC2$) $P(\hbar\omega;A_{T\Pi})$ increases with $\hbar\omega$ and becomes positive in the high-energy tail. ($AC3$) $P(\hbar\omega;A_{T\Sigma})$ is positive but much less than unity in the low-energy tail. ($AC4$) $P(\hbar\omega;A_{T\Sigma})$ decreases as $\hbar\omega$ increases and becomes negative in the high-energy tail.

A static lower symmetry caused by the vacancy can scarcely explain the features $A1$, $A3$, $A4$, $C3$, and $C4$. The JTE, on the other hand, cannot explain the features $A2$, $C1$, and $C2$ as well as the existence of the two emission bands, $C_{T\Sigma}$ and $C_{T\Pi}$, related to the C excited state.[1,4] The features are, however, however, consistent with the assumption that the excited state is mainly distorted by the JTE and is slightly perturbed by the vacancy in the nearest-neighbor position. Let us try to understand the features on the basis of this assumption. We shall first consider the problem in the $\epsilon_g(Q_2, Q_3)$ subspace,[1,4] because the degree of polarization as a function of azimuthal angle in the (100) plane becomes zero in the [011] and [0$\bar{1}$1] directions. Use is made of Russell-Saunders coupling and linear electron-lattice interaction (JTE) which is reasonably small as compared with the spin-orbit interaction.[1,13,14] Then, the $\Gamma_4^-({}^3T_{1u}$ or ${}^1T_{1u})$ adiabatic potential energy surface consists of three intersecting paraboloids P_x, P_y, and P_z, which must have three tetragonal minima.[1,4] These tetragonal minima may not be equivalent because of a lower symmetry due to the vacancy. If the perturbation of the vacancy, V, is assumed to be so small compared with the JTE that only the vacancy in the nearest-neighbor or next-nearest-neighbor position may be effective, two cases are conceivable: (a) One of the three minima is made shallower by $2|\Delta|/3$ and two of them are deepened by $|\Delta|/3$, and (b) two are made shallower by $|\Delta|/3$ and one is deepened by $2|\Delta|/3$. Here $\Delta = -d/2$ for $\Gamma_4^-({}^3T_{1u})$ and $\Delta = d$ for $\Gamma_4^-({}^1T_{1u})$, where d represents the splitting of the t_{1u} orbital and is given by[16]

$$d = (\tfrac{3}{2})\langle t_{1u,\sigma}|V|t_{1u,\sigma}\rangle = -3\langle t_{1u,\pi}|V|t_{1u,\pi}\rangle.$$

If the t_{1u} molecular orbital is well localized, d may be negative when the vacancy is in the nearest-neighbor position and positive when in the next-nearest-neighbor position.

Let us calculate the polarization spectra. Use is made of the Franck-Condon principle and the very simplified assumptions on the relaxation process used in Ref. 4. Since the exciting light is polarized parallel to the [001] direction, the photon energy is given by the energy difference between the ground and excited P_z paraboloids, i.e.,

$$\hbar\omega = E_0 + 2\Delta/3 + 2(B/\sqrt{3})Q_3 \quad \text{for } P_{z\Sigma},$$

and

$$\hbar\omega = E_0 - \Delta/3 + 2(B/\sqrt{3})Q_3 \quad \text{for } P_{z\Pi}.$$

Case (a) corresponds to $\Delta > 0$, and Case (b) corresponds to $\Delta < 0$. The sign of B does not affect the following discussion. Simple but tedious calculations similar to those made in Ref. 4 give the polarization spectra,

$$P(u, \delta; \Sigma \text{ or } \Pi) = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}).$$

Here $I_{\parallel}$ and $I_{\perp}$ are functions of

$$u = (\hbar\omega - E_0)/[4(B\sqrt{3})^2 kT]^{1/2},$$

and

$$\delta = \frac{2\Delta/3}{[4(B\sqrt{3})^2 kT]^{1/2}}.$$

For example, for the Σ emission and in the case of $u < 0$, these are given by

$$I_{\parallel} = \tfrac{1}{2}\{1 - \Phi(\sqrt{3}u)\}\exp\{-(u-\delta)^2\},$$

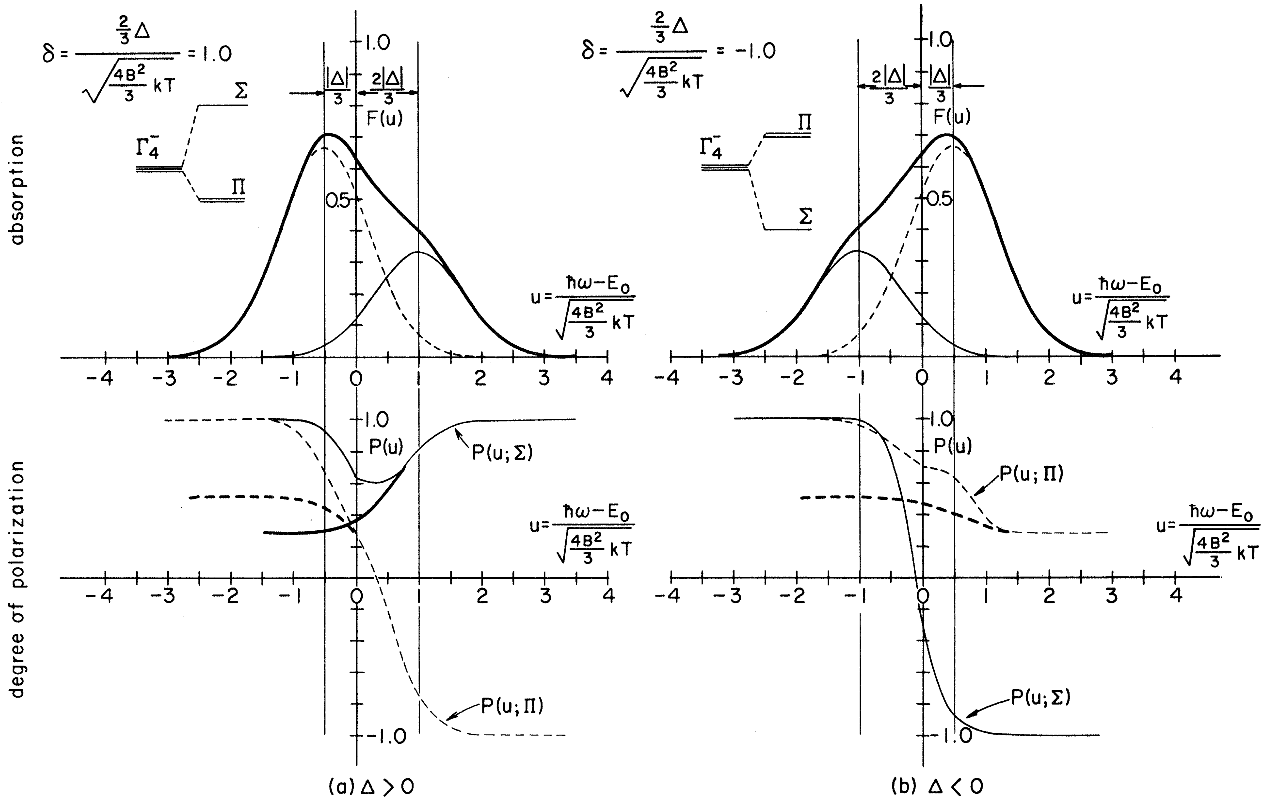
$$I_{\perp} = \tfrac{1}{4}\{1 + \Phi(\sqrt{3}(u-\delta/2))\}\exp\{-(u+\delta/2)^2\},$$

where

$$\Phi(v) = (2/\sqrt{\pi})\int_0^v \exp(-t^2)dt.$$

In Fig. 2 are shown $P(u, \delta; \Sigma \text{ or } \Pi)$ for $\delta = \pm 1$. The absorption band is also given in the figure.[4,13] Note that the absorption band shows only a vague shoulder even when $|\delta|$ is as large as 1 ($B^2 \sim 3$ eV,[14] $T \sim 30°$K,[15] and $\Delta \sim 0.15$ eV), i.e., even when the splitting due to the vacancy is comparable with the half-width due to the interaction with the ϵ_g mode. This shoulder due to the effect of the vacancy may become further obscured by the interaction with the τ_{2g} mode which causes the well-resolved structure of the absorption band.[13]

Now we shall consider the effect of the τ_{2g} mode on the polarization spectra. The effect of the τ_{2g} mode can be considered to mix the P_x, P_y, and P_z paraboloids because the τ_{2g} mode has off-diagonal elements.[4] This mixing is especially important for excitation in the low-energy tail of the



(a) Δ > 0

(b) Δ < 0

FIG. 2. Polarization spectra with $\delta = \pm 1.0$ obtained theoretically. Thin lines were calculated by considering the interaction with the ϵ_g mode only. The interaction with the τ_{2g} mode was taken into consideration qualitatively; in most cases, the interaction causes the depolarization in the low-energy tail as shown schematically by thick lines. Note, however, that such depolarization does not occur in the case of $P(u;\Sigma)$ for $\Delta < 0$. For reference, the absorption-band shape is also given in the upper part, which was calculated by considering the interaction with the ϵ_g mode only.

absorption band, since, without the interaction with the τ_{2g} mode, the system inevitably arrives at the M_z minimum and hence the degree of polarization is unity.[4] The interaction with the τ_{2g} mode makes it possible that the system may arrive at the M_x or M_y minimum. The following are the main results of this effect: (a) For $\Delta > 0$, both $P(u;\Pi)$ and $P(u;\Sigma)$ become much less than unity in the low-energy tail. However, $P(u;\Sigma)$ may be smaller than $P(u;\Pi)$, because the probability for the system to arrive at the $P_{z\Pi}$ paraboloids is higher than that for the system to arrive at $P_{z\Sigma}$, and moreover because the Σ emission produced by the system which arrives at $P_{z\Pi}$ is always polarized perpendicularly to the z axis. Thus, roughly speaking, $P(u;\Sigma)$ and $P(u;\Pi)$ in Fig. 2 may be modified as shown by thick lines. (b) For $\Delta < 0$, $P(u;\Pi)$ also becomes much less than unity, because the system which arrives at $P_{z\Sigma}$ and $P_{z\Pi}$ may relax to $M_{x\Pi}$ and $M_{y\Pi}$ and may produce the Π emission polarized perpendicularly to the z axis. However, $P(u;\Sigma)$ still remains unity, because the system mainly arrives at $P_{z\Sigma}$ when excitation is in the really low-energy tail of the absorption bands. The interaction with the τ_{2g} mode makes it possible that the system may arrive at $M_{x\Pi}$ and $M_{y\Pi}$, but the emission from $M_{x\Pi}$ and $M_{y\Pi}$ is the Π emission. Therefore, so far as the Σ emission is observed, it is completely polarized in the z direction.

In this way, the characteristic features of polarization spectra are qualitatively explained by assigning Case (a), $\Delta > 0$, to $\Gamma_4^-({}^3T_{1u})$ and Case (b), $\Delta < 0$, to $\Gamma_4^-({}^1T_{1u})$, i.e., by considering $d < 0$. Quantitatively, however, there are difficulties. For example, we cannot explain why the separation between $A_{T\Pi}$ and $A_{T\Sigma}$ is larger than that between $C_{T\Sigma}$ and $C_{T\Pi}$. The present analysis shows that the former should be one-half of the latter. Moreover, the interaction with the τ_{2g} mode is not treated quantitatively. Despite the fact that the discussion is necessarily highly qualitative, it can be concluded that the perturbation of a vacancy demonstrates the importance of the Jahn-

Teller tetragonal distortion due to the interaction with the ϵ_g mode and of the depolarization due to the interaction with the τ_{2g} mode. It should be noted that, since the polarization of luminescence is caused by the JTE, the degree of polarization as a function of azimuthal angle gives little information on the direction in which the vacancy exists. In fact, since $d<0$ as concluded above, the vacancy may exist in the nearest-neighbor position although the degree of polarization as a function of azimuthal angle in the (100) plane becomes zero in the [011] and [0$\bar{1}$1] directions.

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Electron-Spin-Resonance Measurements of the Spin Susceptibility of Heavily Doped *n*-Type Silicon*

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The results of relative spin-susceptibility measurements as a function of donor concentration are reported for heavily doped *n*-type silicon. It is shown that, at liquid helium temperatures, the susceptibility decreases with impurity concentration for samples in the impurity-band region. At still higher concentrations, the susceptibility is well described by the $(\text{concentration})^{1/3}$ law expected for a degenerate electron gas.

Results of ESR measurements of the spin susceptibility associated with heavy dopings of phosphorus impurities in silicon have been reported[1-3] and interpreted in terms of combined impurity-band and localized-electron models. Several anomalous features of these results, which appeared at liquid helium temperatures, have been treated with some skepticism[4] primarily because of (1) the inherent inaccuracy of an ESR method, which in principle requires a double integration of the observed resonance line and a comparison with the broad line of a $CuSO_4 \cdot 5H_2O$ "standard" sample, and (2) the absence of similar anomalies in subsequent static susceptibility measurements.[2,5]

This Letter presents the results of our own ESR susceptibility measurements which are in disagreement with those previously reported[1] but are qualitatively consistent with other related experimental data.[4] Our data were obtained through the use of an X-band (~9.1 GHz) TE_{104} double-sample cavity equipped with a modulation "switch." The latter device utilized the fact that a reduction in the amplitude of the ~2-kHz magnetic modulation field at one of the two sample sites reduces the contribution of the sample at that site to the total observed signal (our spectrometer detected synchronously to this modulation). Thus by recording the two overlapping sig-