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F_A(Li) centers in mixed crystals of alkali halides

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The emission and absorption of F_A(Li) centers in mixed crystals of KCl and KBr have been studied from 1.6 to 100 K at atmospheric and high pressures. While only one pair, F_{A1} and F_{A2}, of absorption bands is observed, two types of emission bands, type I and type II, are obtained. The relative intensities of the type-I and type-II emissions depend both on the composition of the solid solution and on temperature. A possible formation mechanism of two relaxed excited states in a complete solid solution is discussed. The energy separation and intensity of the F_A absorption band (F_{A1} and F_{A2}) in the $KCl_{1-x}Br_x$:Li system are observed under various pressures. Information about the off-center behavior in the mixed crystals is obtained from the pressure dependence of the separation between F_{A1} and F_{A2} absorption. The pressure variation of intensity in type-I and type-II emissions is also measured. These results show a different pressure effect on the relaxation processes of the two types of emission: the type-II emission is scarcely affected by the applied pressure contrary to a considerable pressure-induced nonradiative transition in the type-I emission. This situation leads us to investigate the relaxation process of the type-II emission under hydrostatic pressure.

I. INTRODUCTION

The F_A(Li) center in KBr is of type-I behavior. The relaxation process after optical excitation is similar to that of the ordinary F centers which retain a single-vacancy configuration. In contrast to this the F_A(Li) center in KCl is of type-II behavior. It relaxes to a saddle-point configuration after optical excitation and shows a narrow emission band at 0.46 eV due to a radically different process from that of type I.[1] As a result of sufficient overlap between the wave functions for the excited and ground states of the relaxed center, the oscillator strength of the luminescence band is quite large, so that the F_A(II) centers are highly suited for laser action.[2]

It is well known that the $KCl_{1-x}Br_x$ system forms a solid solution through the composition range.[3,4] In this mixed system, what kind of relaxed configurations and emission band are expected?

In the first half of this paper, the emission and absorption spectra of F_A centers in $KCl_{1-x}Br_x$ mixed crystals are studied and compared with those of the F centers in the mixed crystals. In the latter half, the pressure effects of the absorption and emission of F_A centers in the mixed crystals are investigated.

II. EXPERIMENTALS

Single crystals of KCl, KBr, and a $KCl_{1-x}Br_x$ solid solution are grown with 1 mol % LiCl or LiBr in the melt by the usual Kyropoulos method in air. $KCl_{1-x}Br_x$ compositions represent doping in the melt. The cleaved blocks of crystals are additively colored to the F-center concentration of $(2-3)\times10^{17}$ cm^3. After the specimen is quenched form 550 °C to room temperature, it is exposed to F light centered at 546 nm at room temperature. In our optical system (composed of a 500-W Xe lamp and a Karl Leiss monochromator, with entrance and exit slit widths of 1.0 and 0.5 mm, respectively) the F_A absorption bands reach their maxima after exposure to F light for 3 min for KCl, 15 min for KBr, and 3–15 min for the $KCl_{1-x}Br_x$ solid solution with different compositions. For the measurement of F centers in the solid solution (which are compared with the F_A centers), crystals having no additional Li^+ ions are used.

The x-ray diffraction patterns of the mixed crystals correspond to those of a solid solution. The high-pressure cell and the experimental apparatus were previously described elsewhere.[5] The homogeneity of the pressure in the sample at low temperature is also discussed in Ref. 5.

III. RESULTS AND DISCUSSION

A. Emission spectra of F_A(Li) centers in solid solution

The emission spectra of F_A centers for the various compositions at 100 K are shown in Fig. 1. Two emission bands, type I and type II, are observed between $x=0.22$ and 0.8. This means that, in this system, two types of relaxed excited states (RES's) are possible even if in a complete solid solution. As the concentration of Br^- ions increases, the F_A(II) emission decreases and the F_A(I) emission increases. On the other hand, F centers of the mixed crystals show only one emission band. The emission-peak energies of F_A and F centers versus composition are shown in Figs. 2(a) and 2(b). As Figs. 1 and 2(a) show, the type-II emission band reaches the highest-peak energy (0.52 eV) in the $KCl_{0.78}Br_{0.22}$:Li crystal. The change of

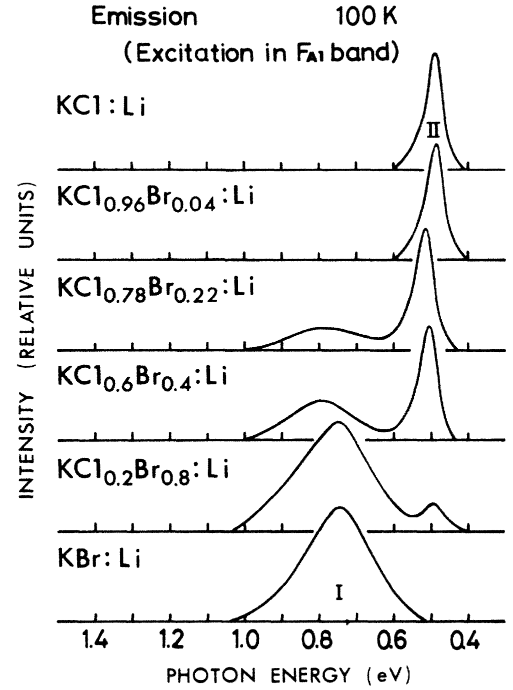

FIG. 1. The emission spectra of F_A centers at various $KCl_{1-x}Br_x$ compositions measured at 100 K.

the peak energy of this band is quite small throughout the various compositions contradicting our expectations for application to a laser source. Its wavelength is shorter by 0.25 μm than the emission peak of type-II emission in KCl:Li, located between the KCl:F_B(II) and KF:Li F_A(II) emission peaks.[6,7] The half-widths of the emission bands of the F_A and F centers are shown in Figs. 2(c) and 2(d).

The absorption peaks of the F_A(Li) and F centers for the different composition of $KCl_{1-x}Br_x$ crystals are also observed at 100 K. The results are shown in Figs. 3(a) and 3(b). Both defects show one kind of absorption behavior, i.e., only one kind of unrelaxed excited state (URES) exists throughout the composition range (a split URES for F_A centers, and an unsplit URES for F centers). The half-widths of the absorption spectra of the F_A and F centers are shown in Figs. 3(c) and 3(d). In the case of F centers, our results agree with earlier data.[3] Next, we have to explain how two kinds of RES's are formed in a complete solid solution. In the environment of the F_A center, as shown in Fig. 4, four halogen ions (shaded) around the Li^+ ion are primarily responsible for the formation of the ionic configuration in the RES. Therefore, the manner in which Cl^- and Br^- are distributed among the four halogen ion sites determines the type of RES configuration (the vacancy and/or saddle-point configuration).

For example, in the $KCl_{0.6}Br_{0.4}$:Li crystal, the type-I and type-II emission intensities are comparable, as shown in Fig. 1. We may consider that the mixing of 40 mol % KBr into KCl corresponds to the replacement of two of the four Cl^- ions with Br^- ions. Roughly speaking, this leads us to the concept that the vacancy configuration and the saddle-point configuration are formed at the same rate.

The energy levels of both F_A(I) and F_A(II) centers are displayed in Fig. 5. As is well known, the KCl:Li-F_A system (not including additional Br^- ions) shows type-II emission. In this system, the initial state of type-II emission (denoted state 1 in the figure) is lower than that of type I (state 3), so that only the type-II emission appears. From the experimental results, we know that the addition

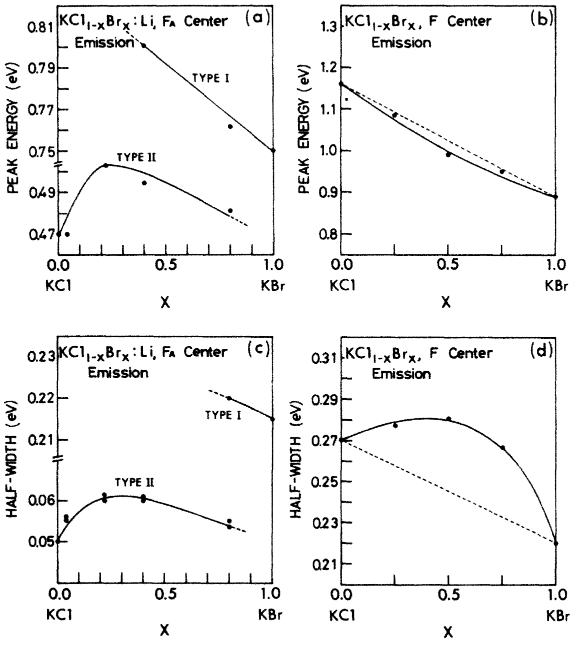

FIG. 2. (a) and (b): Emission-peak energy of F_A and F centers versus compositions at 100 K. (c) and (d): Half-width of emission of F_A and F centers versus compositions at 100 K.

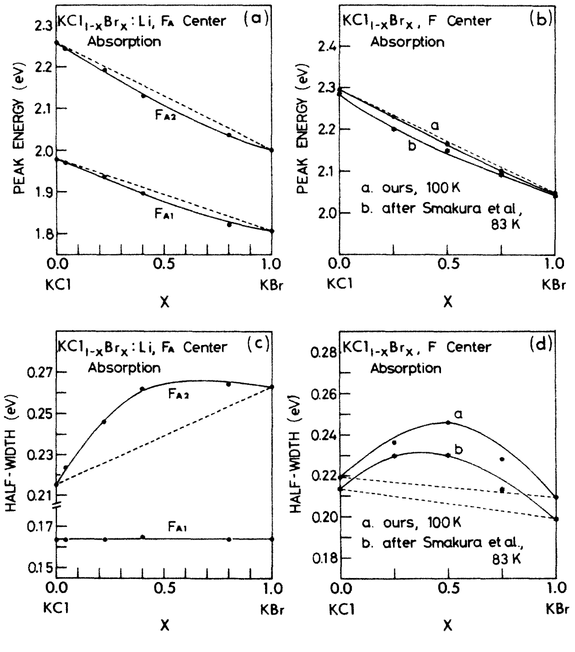

FIG. 3. (a) and (b): Absorption-peak energy of F_A and F centers versus compositions at 100 K; (c) and (d): Half-width of absorption of F_A and F centers versus compositions at 100 K.

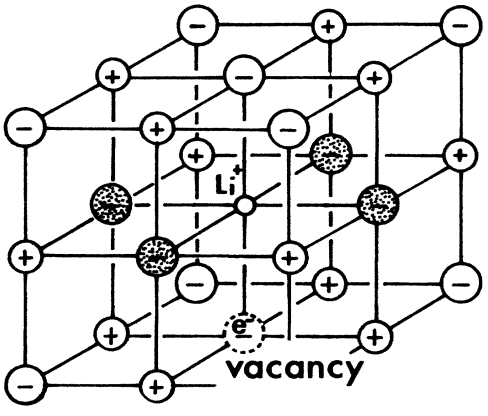

FIG. 4. Model of F_A(Li) center.

of Br^- ions makes it difficult to form the saddle-point configuration; as Br^- ions are added, the initial state of type-II emission (state 1) lifts and at last surpasses that of type I (state 3). This situation increases the F_A(I) emission in the mixed systems.

Of course, the average distribution of Cl^- and Br^- ions over all anion lattice points may also influence the relaxed configuration: the change of mean lattice character through the $KCl_{1-x}Br_x$ mixture may influence the relaxed configuration. The introduction of Br^- ions into the KCl:Li system will change a lattice constant and moreover give a strain to the lattice. Though we cannot say anything decisively, the above situation will not influence the formation of the saddle-point configuration, since the type-II emission is scarcely affected by the applied pressure as described in Sec. III B. Among the solid solutions composed of various compositions, the $KCl_{0.6}Br_{0.4}$:Li crystal shows the most remarkable temperature dependence. Under lowering of the temperature from 73 K, type-II emission decreases and type-I emission increases. At 1.6 K, the former almost vanishes. It suggests that the relaxation process to the saddle-point configuration requires some thermal-activation energy.

Recently, Yang and Luty[8,9] studied the temperature dependence of the emission of the F_B(II) center in the KCl:Na crystal. Their results on the behavior of 1.3 and 2.4 μm emissions are very similar to our results (Fig. 6). They give an essential discussion concerning the relaxation process. The point of their discussion is that the system during relaxation has to pass through the type-I RES first, before reaching the final saddle-point configuration. They estimated the thermal-activation energy for F_B(II) emission at 2.4 μm from the temperature dependence of the emission intensity. It was attributed to the height of potential barrier between the F_B(I) and F_B(II) RES. Furthermore, they measured time-resolved emission decay curves (at about 1.0 μm) in the KCl:Li-F_A center before and after optical aggregation, and found that an emission of ~1.0 μm still exists with a very short lifetime even after almost complete optical aggregation. From this they conclude that the system during relaxation does not go directly to the saddle-point configuration.

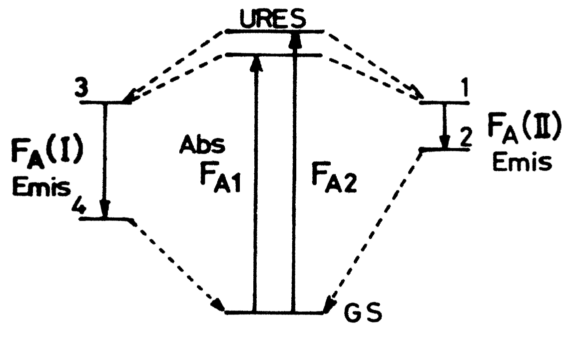

FIG. 5. Energy levels of F_A(I) and F_A(II) centers. GS denotes the ground state.

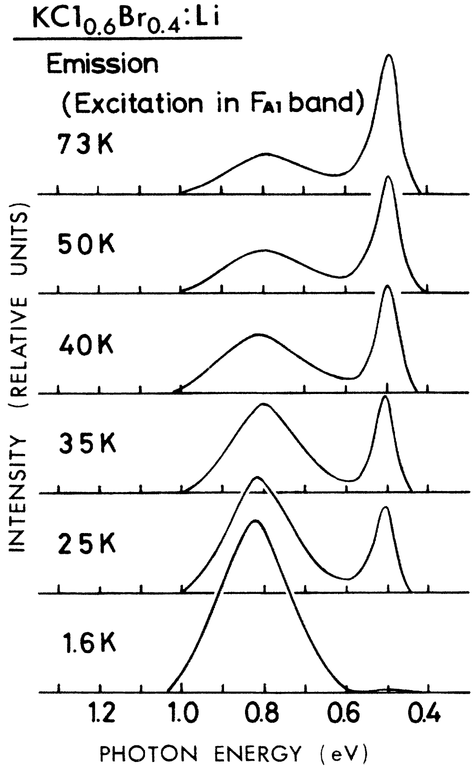

FIG. 6. Temperature dependence of emission spectra in the $KCl_{0.6}Br_{0.4}$:Li system.

B. Pressure effects on the F_A(Li) centers in solid solution

1. *Absorption bands*

The separation of the F_A band peaks (F_{A1} and F_{A2}) in the $KCl_{1-x}Br_x$:Li systems under pressure variation is observed at 1.6 K (Fig. 7). In KCl:Li, F_A band splitting increases with pressure up to 3.5 kbar, decreases rapidly in the pressure range from 3.5 to 7 kbar, and then increases again above 7 kbar.[10] It is well known that the Li^+ ions in the KCl:Li-F_A system give rise to off-center behavior with the displacement along the ⟨110⟩ direction from the normal cation site.[1] The abrupt change in the splitting suggests the change of the ionic configuration in the ground and unrelaxed excited states under applied pres-

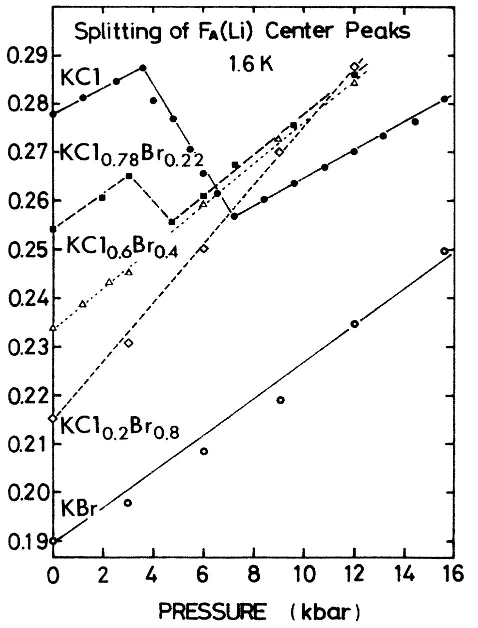

FIG. 7. Peak separation of the F_A absorption band in the $KCl_{1-x}Br_x$:Li system versus pressures at 1.6 K.

sure, i.e., the transition of the Li^+ ion to the on-center at 4—7 kbar. In the $KCl_{0.78}Br_{0.22}$:Li-F_A system, discontinuous change due to transition from off- to on-center appears at lower pressures than that in KCl:Li. This indicates that the Li^+ ion in the F_A center in the $KCl_{0.78}Br_{0.22}$:Li crystal is shallower off-center than that in the KCl:Li system. In the crystals doped with more Br^- ions, the splitting energies increase monotonically. Therefore, Li^+ ions in these systems may be in the normal site even at atmospheric pressure. The increasing of splitting with pressure after transition from off- to on-center suggests that the effect of the perturbation caused by the Li^+ ion increases with pressure. The character of the core of the ligands is more reflected in the electronic structure of the F_A center as they are compressed. On the other hand, as they expand, their contribution to the electronic structure depends more on their ionic charge. (It is probable that the Li^+ ion moves closer to the vacancy site than the other potassium ligands with increasing pressure.)

The band shapes of F_A absorptions under pressure were measured in three crystals: KCl:Li, KBr:Li, and $KCl_{0.6}Br_{0.4}$:Li (Fig. 8). With increasing pressure, the absorption intensity (area) of the F_{A1} band decreases, accompanied by an almost complementary increase of the absorption of the F_{A2}. In the mixed crystal, the F_{A1} band decreases even more with pressure. The asymmetric property of the distributions of trapped electrons which is caused by the core differences of the ligand ions Li^+ and K^+) may be enhanced by shrinkage of the ligand ions under external pressure. This situation is roughly considered as follows: Mixing of the *s* state in the excited *p* state (the final state of F_{A1} absorption) and of the *p* state in the ground state may be enhanced by the shrinkage of the ligand ions. It results in a decrease in dipole transition in the F_{A1} absorption and an increase of it in the F_{A2} absorption.

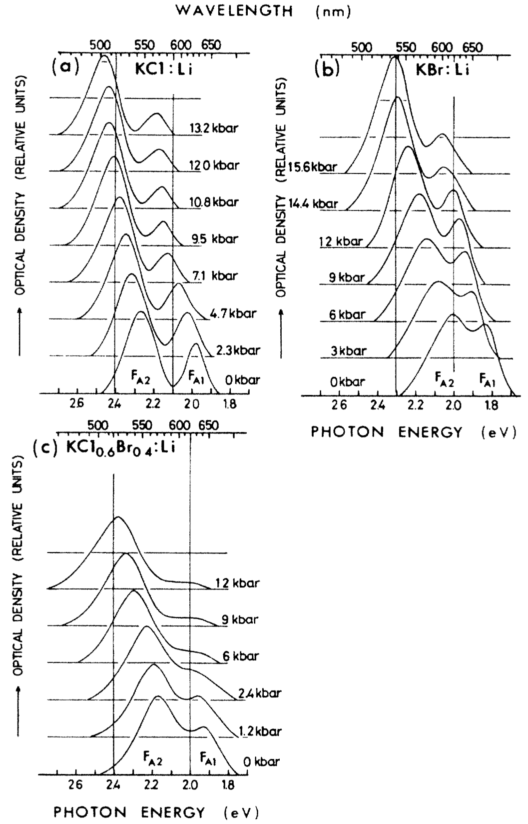

FIG. 8. Pressure dependence of F_A(Li) absorption spectra of KCl, KBr, and $KCl_{0.6}Br_{0.4}$ at 1.6 K.

2. Emission bands

The effects of pressure on the type-I and type-II emission bands are shown in Fig. 9. In type-II emission [Fig. 9(a)], the peak position and the emission intensity are almost independent of applied pressure up to 18 kbar (in the NaCl structure). Furthermore, the type-II emission remains almost unchanged even after the phase transition. (Above 18 kbar the phase shows CsCl structure.) This feature suggests that the RES in the KCl:Li-F_A center still keeps the saddle-point configuration after the NaCl→CsCl phase transition. Although the type-II emission intensity observed in the mixed crystal at 1.6 K is extremely weak, as shown in Fig. 6, the narrowly observed type-II emission shows a behavior similar to that of the KCl:Li-F_A emission up to 5 kbar, i.e., the peak position and emission intensity are almost independent of pressure [Fig. 9(c)].

For the type-I F_A emission, we can observe the same pressure effects as for the F-center emission: a blue shift of the peak position and decrease of the intensity [Figs.

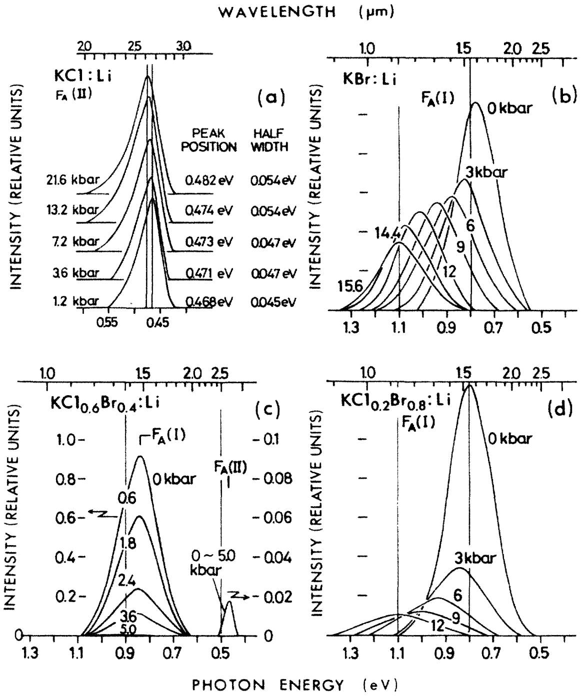

FIG. 9. Pressure dependence of F_A(Li) emission spectra of KCl, KBr, $KCl_{0.6}Br_{0.4}$, and $KCl_{0.2}Br_{0.8}$ at 1.6 K.

9(b) and 9(d)]. This indicates that the relaxation process of type-I F_A emission is essentially the same as that of F emission. The decrease of the emission intensity may be due to the dynamical nonradiative transition (NRT).[11]

A most curious feature is the rapid decrease in type-I emission of the $KCl_{0.6}Br_{0.4}$:Li system [Fig. 9(c)]. It vanishes before showing any peak shifts. In the $KCl_{0.2}Br_{0.8}$:Li system (the type-II emission almost vanishes and type I is dominant), the emission intensity also shows a rapid decrease. The effect of pressure on the F emission in mixed crystals was also observed, and no difference was found between the single and mixed systems. A clear difference in the pressure effect of the emission between the F_A(I) and F centers in mixed crystals is that the former shows fast decrease with pressure. It is interesting that in spite of the rapid decrease of the type-I emission [the pressure-induced nonradiative transition (NRT)], the type-II emission scarcely decreases under pressure. This feature suggests that the relaxation from URES to the saddle-point configuration occurs without suffering from dynamical NRT. As described above, this process requires thermal-activation energy. It means that the system relaxes to the saddle-point configuration assisted by thermal activation, passing through an intermediate relaxed vacancy configuration as in the case of the F_B(II) emission. In the F_B(II) emission, the above intermediate RES is identified with the type-I RES. In the present case, however, the fact that this process is one not suffering from the pressure-induced NRT requires a further interpretation of the details of relaxation under high pressures. It is desirable to have more experimental information, for example, for the time-resolved emission decay. We are planning to have a more detailed experiment overcoming the difficulty of the smallness of samples in a high-pressure cell.

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[1] F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. 3.
[2] L. F. Mollenauer and D. H. Olson, Appl. Phys. Lett. **24**, 368 (1974); J. Appl. Phys. **46**, 3109 (1975).
[3] A. Smakula, N. C. Maynard, and A. Repucci, Phys. Rev. **130**, 113 (1963); J. Appl. Phys. Suppl. **33**, 453 (1962).
[4] G. Miessner, Z. Phys. **134**, 576 (1953).
[5] K. Asami and M. Ishiguro, J. Phys. C **15**, 4193 (1982).
[6] N. Nishimaki, Y. Matsusaka, and Y. Doi, J. Phys. Soc. Jpn. **33**, 424 (1972).
[7] L. F. Mollenaur, B. A. Hatch, and D. H. Olson, Phys. Rev. B **12**, 731 (1975).
[8] Y. H. Yang and F. Luty, International Conference on Defects in Insulating Crystals, Utah, 1984 (unpublished), p. 496.
[9] Y. H. Yang, Ph.D. thesis, The University of Utah, Salt Lake City, 1984.
[10] K. Asami and M. Ishiguro, Phys. Status Solidi B **120**, K205 (1984).
[11] K. Asami, T. Naka, and M. Ishiguro, Phys. Rev. B (to be published). The energies of the absorption final state and the intersection of adiabatic potential curves are discussed using a simple two-level model under different pressures.