F CENTERS PROPERTIES AND PHASE TRANSITIONS ; KCN AND NaCK

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KCN and NaCN crystals show many interesting properties which arise from the molecular character of the CN~ ion group. From temperatures just below the melting point down to a critical temperature **3?i (l68** K for KCN and 288 K for NaCN) these crystals have the NaCl structure, with rapid reorientation of the CN~ group in the cubic crystalline field. A structural phase transition occurs at Tj, with ferroelastic ordering of the CK~ ions. The crystal symmetry point group changes from cubic (0^) to orthorhombic (D_2h)« At a second critical temperature T_2 (83 K for KCN and 172 K for NaCN) the electric dipoles of the CN~ ions become oriented in an antiparallel way, leaving the crystal in an antiferroelectric state.

The optical properties of F centers in KCN and NaCN were measured in the temperature range from 300 K down to *h.2* K. The single gaussian shaped absorption band in the cubic phase splits into three components at the temperature Tj, but no change in the first moment of the whole band was observed within our experimental errors. Between Tj and T_2 the F band remains nearly unchanged. Below T_2, a marked blue shift of the low energy component was observed, whereas the other two remained nearly unchanged. Also a **Bmall** absorption band in the near infrared appeared below T_2. The position of the observed absorption bands are shown in the Table.

The luminescence of F centers in KCN was also measured. The lifetime of the relaxed excited state in KCN is 21.5 ± 2 nsec at *k.2 K,* its value decreasing with the increasing temperature. No luminescence from F centers in NaCN crystals was detected.

The overall behavior of the F band is explained by the symmetry change of the crystalline structure at Ti and by the local electric field which appears below T_2. The spontaneous deformation AQ of the cubic cell at Ti can be decomposed in the cubic symmetry in two deformations AQ_{31} and AQ_{53} which transforms respectively like the basis functions $(2z^2 - x^2 - y^2)$ and

(xy) of the and r| irreductihle representations of the cubic group [1] . In KCN, for example, AQ_{31} « o,oU a and AQ_{53} - 0,03 a, where a is the cubic lattice parameter. To the first order in AQ the strain Hamiltonian of the P center predicts a splitting of the excited state as shown in the figure, with no change in the first moment of the whole F band.

Below T_2, the local electric field which appears along 'the z axis will only mix the 2s (r*) and $2p_z$ (r^) states leaving unperturbed the $2p_x$ *(T^)* and 2p (T^) states. The small band which grows below T_2 can be assigned to the Is -*- 2s transition, which becomes partially allowed by the field mixing. Assuming the same dipole matrix element $<2s|z|2p_z>$ of F centers in KCN and KBr [2] , the local field in KCN can be estimated as ^ 10^7 V/cm.

Uniaxial stress experiments in order to induce a single domain crystal are under way so that more information can be obtained from polarisation measurements.

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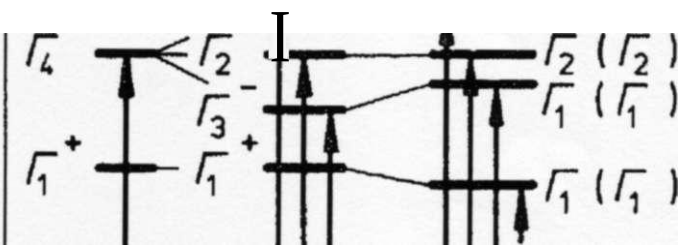
[1] G.H. Henry and CP. Slichter, in "Physics of Colour Centers" Ed. W.B. Fowler, Academic Press, N.Y. (1968).

[2] U.M. Grassano, G. Margaritomdo and R. Rosei, Phys. Rev. B2, 8, 3319 (1970).

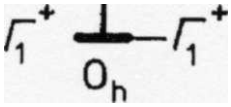
T>T $T_1>T>T_2$ $T<T_2$

	KCN	NaCN
ε_z (Γ_1)	$2{,}09_7$	$2{,}13_1$
ε_y (Γ_2)	$2{,}20_3$	$2{,}34_0$
ε_x (Γ_4)	$2{,}35_0$	$2{,}54_0$



£2s(ri)

TABLE



D_{2h} /7I/7)

C_{2v}(or C_2)