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 $T_1$ (168 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 $T_1$, with ferroelastic ordering of the CK⁻ ions. The crystal symmetry point group changes from cubic ($O^h$) 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 1.2 K. The single gaussian shaped absorption band in the cubic phase splits into three components at the temperature $T_1$, but no change in the first moment of the whole band was observed within our experimental errors. Between $T_1$ 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 small 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 1.2 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 $T_1$ and by the local electric field which appears below $T_2$. The spontaneous deformation $AQ$ of the cubic cell at $T_1$ can be decomposed in the cubic symmetry in two deformations $AQ_{31}$ and $AQ_{53}$ which transforms respectively like the basis functions $(2z'-x'-y')$ and $(x'-y')$. 
(xy) of the irreducible representations of the cubic group [1]. In KCN, for example, \( \Delta Q_{11} \approx 0.001 \) \( a \) and \( \Delta Q_{22} \approx 0.03 \) \( a \), where \( a \) is the cubic lattice parameter. To the first order in \( \Delta Q \) 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 \( T_1 \), the local electric field which appears along the \( z \) axis will only mix the \( 2s \) (\( r^s \)) and \( 2p \) (\( r^p \)) states leaving unperturbed the \( 2p \) (\( T^p \)) and \( 2p \) (\( T^p \)) states. The small band which grows below \( T_1 \) can be assigned to the \( 1s \to 2s \) transition, which becomes partially allowed by the field mixing. Assuming the same dipole matrix element \( <2s|z|2p> \) of F centers in KCN and KBr [2], the local field in KCN can be estimated as \( 1 \times 10^7 \) 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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\[
\begin{array}{c|c|c}
\text{KCN} & \text{NaCN} \\
\hline
\varepsilon_z (\Gamma_1) & 2.097 & 2.131 \\
\varepsilon_y (\Gamma_2) & 2.203 & 2.340 \\
\varepsilon_x (\Gamma_4) & 2.350 & 2.540 \\
\end{array}
\]

\( \Delta_{2s}(ri) \)

**TABLE**

\[
\begin{array}{c|c}
\text{D}_{2h} & C_{1v} \text{(or } C_{1}) \\
\end{array}
\]