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SPECIFIC HEAT MEASUREMENTS OF THE ANTIPERROELECTRIC  
PHASE TRANSITION IN THE MIXED SYSTEM  $\text{KCN}_x\text{Cl}_{1-x}$

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**ABSTRACT.** The specific heat of  $\text{KCN}_x\text{Cl}_{1-x}$  mixed crystals was measured for four chlorine concentrations between  $x=0,90$  and  $x=1,00$ . The entropy change  $\Delta S$  and critical temperature  $T_c$  were obtained and the results are discussed in terms of the orientational motion of the  $\text{CN}^-$  molecular ions. *Resumo*

**RESUMO.** O calor específico de cristais mistos de  $\text{KCN}_x\text{Cl}_{1-x}$  foi medido para quatro concentrações de cloro entre  $x=0,90$  e  $x=1,00$ . A variação de entropia  $\Delta S$  e a temperatura crítica  $T_c$  foram obtidas e os resultados são discutidos em termos do movimento orientacional dos íons moleculares  $\text{CN}^-$ . *Resumo*

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\* Work partially supported by FINEP, CNPq and CAPES

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**INTRODUCTION**

Phase transitions in pure Alkali cyanides received considerable interest along the last twenty years. For these ionic-molecular crystals the high temperature phase has the cubic symmetry in which the negative molecular ion is reorienting rapidly in the multiple potential well of the anion site. A structural first order phase transition occurs below room temperature, changing the symmetry from cubic to orthorhombic<sup>(1)</sup>. This transition is related to the preferential alignment of the  $CN^-$  molecular ions in a parallel (ferroelastic) way leading a residual head and tail disorder. Potassium and sodium cyanides presents another order-disorder phase transition at lower temperatures related to the alignment of the electric dipoles of the  $CN^-$  radicals in an antiferroelectric state<sup>(2)</sup>. Neutron scattering, optical absorption in the Infrared, Raman and Brillouin scattering, specific heat, dielectric loss and ESR measurements provided a rich ensemble of experimental data relating the phase transitions to the coupled translational and rotational motions of the cyanide ions<sup>(3)-(8)</sup>.

More recently, much attention has been paid to the study of solid solutions of alkali cyanides and alkali halides. These solutions can be grown in any desired concentration of the constituents for almost all alkali halides, specially the

Chlorides and Bromides. Dilution of the  $\text{CN}^-$  dipole concentration by halide substitution gradually lowers the ferroelastic transition temperature until a critical  $\text{CN}^-$  concentration,  $x_c$ , is reached, where all indications of a long range ordered phase disappear abruptly ( $x_c=0.80$  for  $\text{K}(\text{CN})_x\text{Cl}_{1-x}$ <sup>(9)</sup>). It has been suggested that crystals with  $x < x_c$  freeze in an orientational glass state<sup>(10) (11)</sup> but more work need to be done in order to completely clarify the nature of this state.

We report here specific heat measurements on  $\text{KCN}:\text{KCl}$  mixed crystals at temperatures below 120K. To our knowledge this is the first direct observation of the behaviour of the antiferroelectric phase transition as a function of the concentration in mixed alkali halide cyanide crystals. The specific heat technique is very suitable in this case, as it probes directly a thermodynamic quantity which presents anomalous behaviour near a phase transition.

#### EXPERIMENTAL

The specific heat measurements were performed in a home - made adiabatic calorimeter suitable for sample weights as small as 200 mg. The temperature was measured with an Allen Bradley carbon resistor and a Picowatt AC resistance Bridge giving a precision of 0.15K and sensibility of 0.02K near

100K. The samples were placed between two alumina plates, one containing the thermometer and the other containing a heater deposited by the thick film technique, and suspended to the calorimeter with nylon threads. For a typical sample of 200 mg the heat capacity of the sample holder, thermometer and heater was always less than 25% of the sample heat capacity.

The samples were cleaved platelets of  $5 \times 5 \times 2 \text{ mm}^3$  size (typically), grown at the crystal growth facilities of the Instituto de Física e Química de São Paulo, São Carlos by the Czochralsky Technique. The reason for using such small samples was to avoid or reduce the concentration gradient which occurs during the growth of the mixed crystal. The cleaved platelets had their smallest dimension along the axis of crystal growth.

The heat capacities were measured by rising the temperature in steps between 1K and 2K, and then the region around the anomaly was measured again in steps smaller than 0,5K.

## RESULTS AND DISCUSSION

The specific heat of  $\text{KCN}_x\text{Cl}_{1-x}$  crystals was measured for four different concentrations:  $x=0.99$ ,  $x=0.98$ ,  $x=0.95$  and  $x=0.90$ . The temperature dependence of the specific heat for  $x=0.99$  shown in figure 1, presents a characteristic lambda peak

at  $T=76.0\text{K}$  corresponding to the antiferroelectric phase transition for this concentration of the halide-cyanide mixture.

In order to separate the normal and anomalous parts of the specific heat, the contributions of the translational motion of the ions (phonons) and the rotational motion of the  $\text{CN}^-$  radical must be subtracted. Since the Debye temperature of pure KCN and KCl in the temperature range of interest differ by only 6%<sup>(2)</sup> we expect the translational part of the specific heat to be unaffected by the dilution of some percent Chlorine ions in the cyanide crystal. Therefore the translational part of the specific heat of the mixed crystals was taken to be the same as for pure KCN. By lack of more detailed information, the contribution of the rotational motion of the  $\text{CN}^-$  ions was taken to be proportional to the  $\text{CN}^-$  concentration and having the same temperature dependence as in pure KCN. We will come back to this point in a latter discussion.

With the assumptions discussed above, the normal and anomalous contributions to the specific heat of mixed halide-cyanide crystals below 100K can be separated. The anomalous part of the specific heat of the mixed crystals are shown in Figure 2, together with that of pure KCN derived from the data of Suga et al<sup>(2)</sup>. The evolution of the antiferroelectric phase transition can be easily observed as well as the onset of the ferroelastic phase transition, whose contribution appears for

$x=0.95$  and becomes dominant for  $x=0.90$ . It should be noted that the observed peak for  $x=0.99$  appears sharper than that of pure KCN. This is probably due to the fact that our temperature steps in the specific heat measurements ( $<0.5\text{K}$ ) were smaller than those of Suga et al ( $\sim 2\text{K}$ ). It can also be observed that the specific heat anomaly becomes broader as the Chlorine concentration increases. This broadening is probably due to the local fluctuations of the Chlorine concentration within the sample, becoming more important as this concentration increases.

The evolution of the entropy change  $\Delta S$  and critical temperature  $T_c$  associated to the antiferroelectric phase transition are shown in figures 3 and 4 respectively. The data for  $x=0.90$  and  $x=0.95$  were obtained by subtracting the tail of the ferroelastic phase transition, being therefore less accurate than those for  $x=0.98$  and  $x=0.99$ . Nevertheless, the existence of a specific heat anomaly associated to the antiferroelectric phase transition in KCN,  $\text{Cl}_{0.90}\text{Br}_{0.10}$  is clearly indicated by the small hump on the tail of the ferroelastic phase transition.

The dependence of  $\Delta S$  and  $T_c$  on the concentration  $x$  shows a much faster decay than predicted by the mean field theory<sup>(12)</sup>. This kind of behaviour was expected since this theory neglects not only pair correlation effects but also

details on the reorientation dynamics of the  $\text{CN}^-$  ions. In fact, the reorientation of the  $\text{CN}^-$  ions at low temperatures depend on the elastic potential barriers and relative energies associated to the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  orthorhombic directions<sup>(8)</sup>. The introduction of Chlorine ions, whose ionic radius is smaller than that of cyanide ions, will probably affect the potential barriers and energy minima of the hindering potential well, making the critical temperature to decrease much faster than that predicted by the mean field theory.

It should be pointed out that the dilution of Chlorine atoms may actually affect somewhat the contribution of the rotational motion of the  $\text{CN}^-$  ions to the specific heat, mainly for the highest chlorine concentrations. However, since the data for these concentrations carry already an uncertainty due to the subtraction of the tail of the ferroelastic phase transition, any correction of the baseline would be a useless refinement.

The fact that the entropy change  $\Delta S$  associated to the antiferroelectric phase transition goes down to zero much faster than the critical temperature raises the question whether the rate of cooling of the sample will affect its physical properties at low temperature. Dielectric loss and I.T.C. measurements in pure cyanides and mixed halide cyanide crystals showed that the reorientation frequency of the cyanide ion



decreases several orders of magnitude below 100K, reaching values of small as  $10^{-1}$  Hz near 40K<sup>(13) (14)</sup>. It is easily seen that the rate of cooling the sample will give rise to a residual entropy at low temperatures unless it follows the same temperature dependence as the reorientation frequency, which is completely unpractical under laboratory conditions. Optical absorption measurements indeed showed a small fraction of  $\text{CN}^-$  ions oriented with its electric dipole opposite to the local electric field even at very low temperatures<sup>(15)</sup>, confirming that the orientational configuration of the  $\text{CN}^-$  dipoles do not correspond to a thermal equilibrium situation. Therefore the residual entropy would explain the small values of  $\Delta S$  observed for  $x=.90$  and  $.95$ .

In conclusion, we can say that the measured specific heat data and transition temperature as function of the concentration are not explained by the mean field theory, and that the disorder introduced by the chlorine ions in the lattice plays an important role as well as the rate of cooling of the sample. Both phenomena are probably the responsible by the strong dependence of the measured entropy change and critical temperature with the Chlorine concentration in



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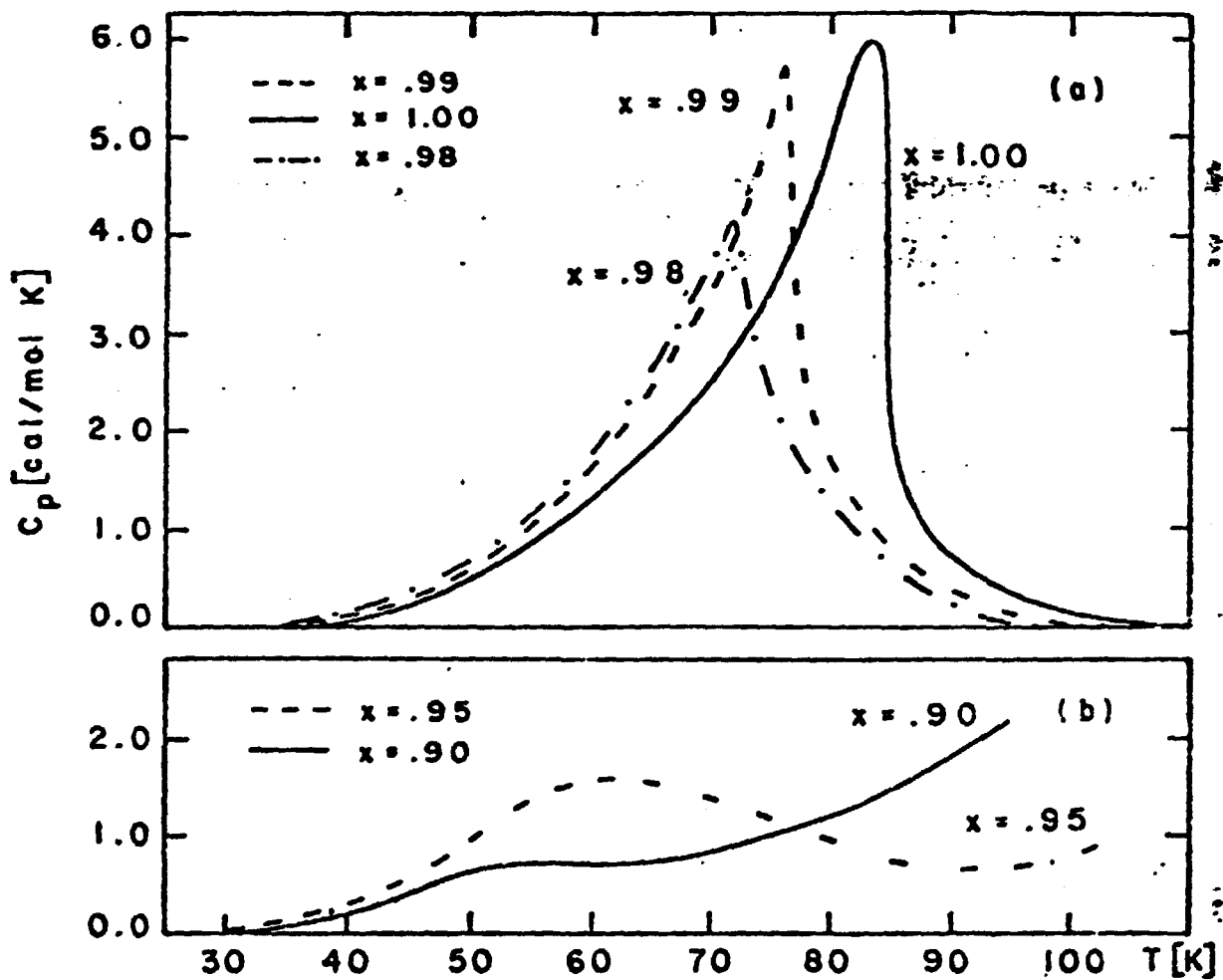
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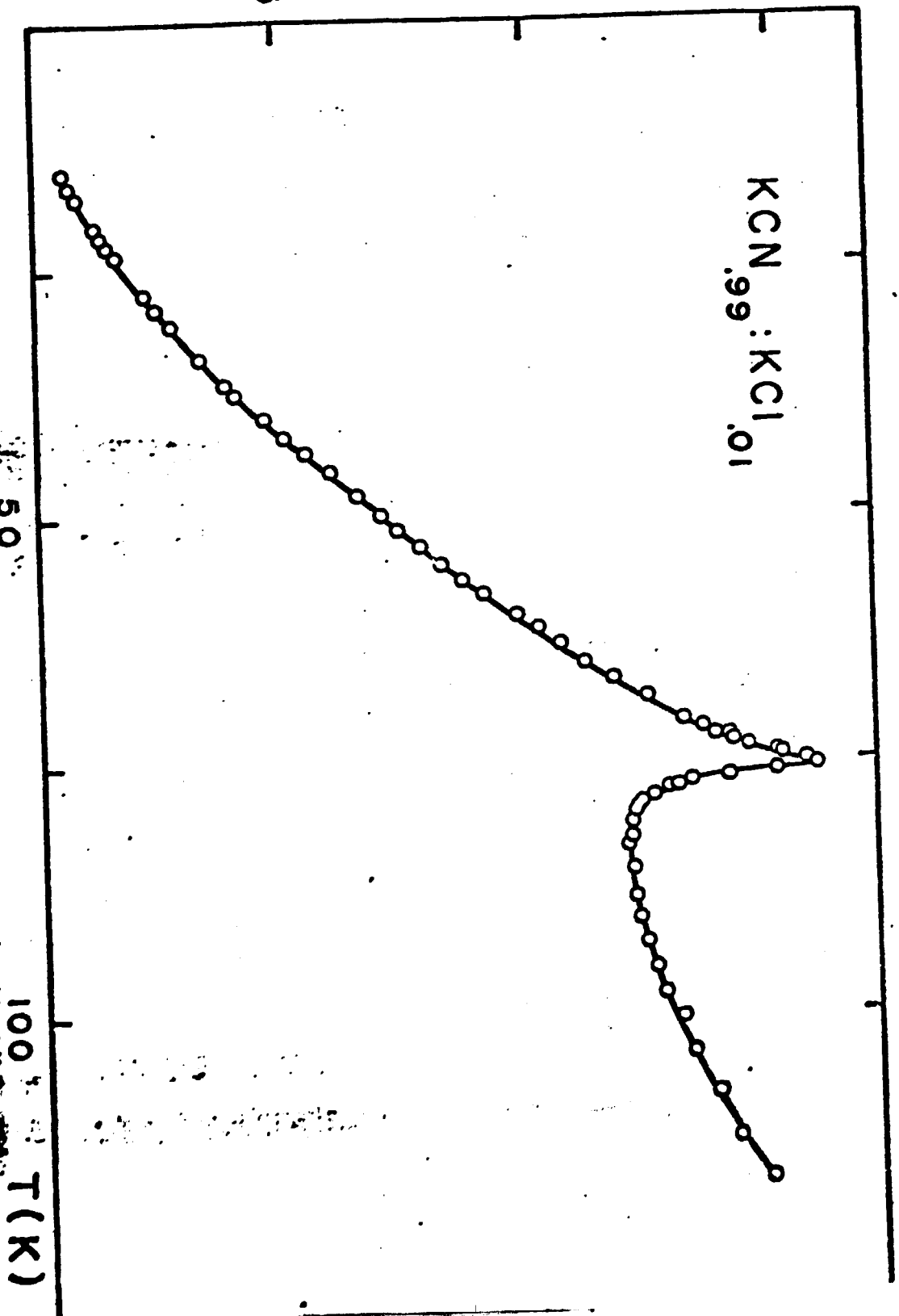
#### FIGURE CAPTIONS

- Figure 1 - Temperature dependence of the specific heat of  $\text{KCN}_{.99}\text{Cl}_{.01}$ . The antiferroelectric transition temperature is  $T_c = 76.0\text{K}$ .
- Figure 2 - Contribution of the ferroelectric and antiferroelectric phase transition to the specific heat of  $\text{KCN}_x\text{Cl}_{1-x}$ . The antiferroelectric contribution is dominant in (a) and less important in (b).
- Figure 3 - Entropy change  $\Delta S$  of the antiferroelectric phase transition as a function of the  $\text{CN}^-$  molar fraction  $x$ .
- Figure 4 - Transition temperature  $T_c$  of the antiferroelectric phase transition as a function of the  $\text{CN}^-$  molar fraction  $x$ .



$C_p$  (cal/mol.K)

KCN<sub>.99</sub>:KCl<sub>.01</sub>



50

100 T (K)

