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LETTER TO THE EDITOR

Group-theoretical description of the 413 K phase transition in KSCN

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Abstract. Primary- and secondary-order parameters are found in the 413 K phase transition of KSCN by symmetry rules. The soft mode polarisation is predicted. A closed form of all the invariants of the free energy is given and used to analyse the existing experimental data.

The change of symmetry $I4/mcm(D_{4h}^{18}) \rightarrow Pbcm(D_{2h}^{11})$ in the phase transition of potassium thiocyanate (KSCN) at 413 K has been known for a long time [1] as well as the fact of an antiferroelectric ordering of the SCN^- anions in the room-temperature orthorhombic phase. The recent structural x-ray studies [2] done in a wide temperature range in both phases of the material and the elastic constants measurements [3] allow for the determination of the physical nature of the order parameters involved in the transition. A systematic group-theoretical description of the phase transition is given below along with a tentative comparison of the theory with the existing experimental data.

The symmetry reduction in the 413 K phase transition of KSCN in terms of the Kovalev tables [4] is as follows:

$$D_{4h}^{18} \rightarrow (k_{15} = (0, 0, 2\pi/c), \hat{\tau}_g(\eta, 0)) \rightarrow D_{2h}^{11}. \tag{1}$$

The low-symmetry group D_{2h}^{11} arises from the one D_{4h}^{18} as a result of the condensation of the two-dimensional irreducible active representation $(k_{15}, \hat{\tau}_g)$ defined by the one-arm star (k_{15}) from the Brillouin zone boundary and by the loaded representation $\hat{\tau}_g$. Here a real form of the active representation is used. To produce the observed change of symmetry only the first component $\eta_1 = \eta$ of the representation must differ from zero.

The total symmetry being reduced by a factor of 4, the three other domains [5] of the low-symmetry phase can be obtained from the point $(\eta, 0)$ in the order parameter space by means of the symmetry operations lost in the transition.

$$\begin{aligned} &\{\varepsilon|\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\}(\eta, 0) = (-\eta, 0) \qquad \{C_{2xy}|0, 0, 0\}(\eta, 0) = (0, \eta) \\ &\{C_{2x\bar{y}}|0, 0, 0\}(\eta, 0) = (0, -\eta). \end{aligned} \tag{2}$$

The projection of the physical representations [6] of different physical quantities onto the active representation defines the real structural distortions allowed by symmetry

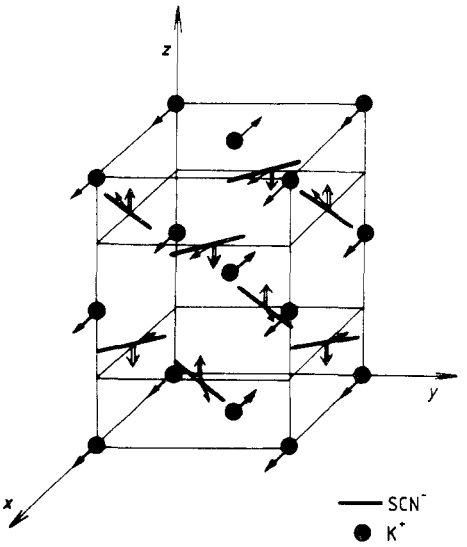

Figure 1. Vectors (↗) and pseudovectors (⇗) involved in primary- and secondary-order parameters in the 413 K phase transition of KSCN.

as the primary-order parameter.

The elementary projection [7] shows that in the case of KSCN the lowest-order contribution to the primary-order parameter comes from the polar vectors attached to the cations and anions.

Denoting by $(v_1, v_2, v_3)_{A(\alpha\beta\gamma)}$ the components of the polar vectors associated with the ion of the type A located at the site $(\alpha\beta\gamma)$ in the tetragonal phase one gets

$$(v_1, v_2, v_3)_{K^+(000)} = (v_K, 0, 0) \qquad (v_1, v_2, v_3)_{SCN^-(\frac{1}{2}0\frac{1}{2})} = (v_A, v_B, 0). \tag{3}$$

The values v_K, v_A and v_B are not determined by symmetry. The corresponding vectors for other ions in the unit cell are obtained from those given in equation (3) by means of symmetry elements of the group D_{2h}^{11}. This is illustrated in figure 1.

The polar vectors describe translational displacements of the ions and/or dipole moments arising at the corresponding sites. The dipoles related to the SCN^- anions come from their head–tail order expresed by the quantity S [2].

Structural distortions which only partly reduce the initial symmetry are called secondary-order parameters [8]. In the case of KSCN the most important quantity of this type is the spontaneous strain. The corresponding physical representation subduces the second power of the active representation so that the phase transition is improper ferroelastic [9] with the faintness index $n = 2$.

There are three independent combinations of the strain tensor components compatible with the symmetry reduction (1):

$$\varepsilon_A = (\varepsilon_{11} + \varepsilon_{22})/2 \qquad \varepsilon_{33} \qquad \varepsilon_B = (\varepsilon_{11} - \varepsilon_{22})/2. \tag{4}$$

The two first combinations leave the initial symmetry unchanged so that they are also responsible for the thermal expansion of the material in the high-temperature phase.

Another secondary-order parameter can be defined by the axial vectors describing angular displacements $\Delta\varphi$ of the anions from their average orientations [110] and [1$\bar{1}$0]

in the tetragonal phase (figure 1):

$$(w_1, w_2, w_3)_{K^+(000)} = (0, 0, 0) \qquad (w_1, w_2, w_3)_{SCN^-(\frac{1}{2}0\frac{1}{4})} = (0, 0, w) \tag{5}$$

where $(w_1, w_2, w_3)_{A(\alpha\beta\gamma)}$ denotes the components of the axial vectors associated with the ion A located at the site $(\alpha\beta\gamma)$.

The free energy of the system must be invariant with respect to the high-symmetry group. Knowing the explicit form of the active representation's matrices one finds all the invariants involving the primary-order parameter components η_1, η_2:

$$I_{mn} = \eta_1^{2n}\eta_2^{2m} + \eta_1^{2m}\eta_2^{2n} \tag{6}$$

where $n, m = 0, 1, 2, \ldots$ and $n \geqslant m$.

Similarly, all the invariants of the elastic free energy are

$$E_{nmqll'pp'} = \varepsilon_A^n \varepsilon_{33}^m (\varepsilon_{13}^2 + \varepsilon_{23}^2)^q (\varepsilon_{13}^2 - \varepsilon_{23}^2)^{2l-l'} \varepsilon_B^{l'} (\varepsilon_{13}\varepsilon_{23})^{2p-p'} \varepsilon_{12}^{p'} \tag{7}$$

with $n, m, q, l, l', p, p' = 0, 1, 2, \ldots$ and $l' \leqslant 2l, p' \leqslant 2p$.

Finally the invariants coupling the primary-order and the secondary-order parameters are following

$$\begin{aligned} M_{abcdemm'm_1m_2m_3nn_1n_2n_3r} &= \varepsilon_A^a (\eta_1^2 + \eta_2^2)^b (\varepsilon_{13}^2 + \varepsilon_{23}^2)^c \varepsilon_{33}^d (\varepsilon_{13}\eta_1 + \varepsilon_{23}\eta_2)^e \\ &\times \varepsilon_B^{2m+m'-m_1-m_2-m_3} (\varepsilon_{13}^2 - \varepsilon_{23}^2)^{m_1} (\eta_1^2 - \eta_2^2)^{m_2} (\eta_1\varepsilon_{13} - \eta_2\varepsilon_{23})^{m_3} \\ &\times \varepsilon_{12}^{2n-2m-m'-n_1-n_2-n_3} (\varepsilon_{13}\varepsilon_{23})^{n_1} (\eta_1\eta_2)^{n_2} (\varepsilon_{13}\eta_2 + \varepsilon_{23}\eta_1)^{n_3} \\ &\times (\varepsilon_{13}\eta_2 - \varepsilon_{23}\eta_1)^{2r-m'} \end{aligned} \tag{8}$$

where all the subscripts of the quantity M must be positive integers (zero included) except that $m' = 0$ or 1, and all the exponents must be non-negative. Additionally $e = 2e' - m_3 - n_3 - 2r + m'$.

The thermal behaviour of KSCN in the tetragonal phase is well accounted for by the usual temperature dependence $A = a(T - T_c)$ of the coefficient multiplying the invariant I_{10} of (6). Indeed, a linear temperature dependence of the inverse of the diffuse x-ray scattering intensity $I^{-1}(k_{15}) \propto (T - T_c)$ [2] witnesses to a generalised soft mode behaviour. The predicted polarisation of the soft mode is given in figure 1. The soft mode is apparently responsible for the anomalies of the thermal coefficients B_{11} [2]. A neutron scattering experiment is needed to reveal dynamical features of the soft mode.

The behaviour of the low-temperature phase of KSCN agrees with the Landau theory only in a close vicinity of the phase transition. At lower temperatures one observes a saturation of the primary-order parameters (see figure 2) that corresponds to almost perfect ordering of the anions' dipoles. In this case an Ising-type free energy is more appropriate [1]. The spontaneous strains (equation (4)) turn out to be proportional to $\eta^2(T)$ (see figure 2) that is accounted for by the invariants linear in strain and quadratic in η_1 and η_2 (equation (8)). However, the same invariants would produce a step-like decrease in the elastic constants [10].

Now the anomalous elastic constants c_{11}, c_{22}, c_{33} are almost perfectly proportional to the spontaneous strains ε_{11}, ε_{22}, ε_{33} respectively. (Their ratios are constant to an accuracy better than 1%, see figure 2.) This indicates a direct elastic constants dependence on the spontaneous strains which makes it necessary to include at least third-order terms of equation (7) into the free-energy expansion.

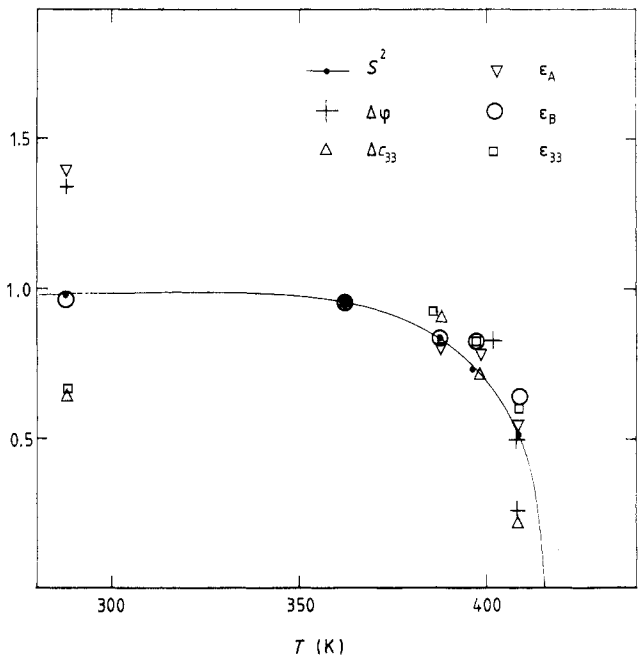

Figure 2. Temperature dependence of primary- and secondary-order parameters. Primary-order parameter: orientational probability (S). Secondary-order parameter: torsions of S–C-bondings ($\Delta\varphi$) (for displacements of K^+ ions see [2]); ε_A, ε_B, ε_{33} (subtracted normal thermal expansion extrapolated from tetragonal phase) and anomalous part of elastic constant (c_{33}) in the low-temperature phase of KSCN.

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