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1990 J. Phys.: Condens. Matter 2 2355

(http://iopscience.iop.org/0953-8984/2/10/003)

J. Phys.: Condens. Matter **2** (1990) 2355–2359. Printed in the UK

Birefringence study of the 415 K phase transition in KSCN

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Received 24 July 1989

Abstract. KSCN shows an order–disorder phase transition at 415 K. Accurate measurements of the birefringence in the temperature range from room temperature to 420 K support the validity of the Ising model with volume-dependent interactions. The temperature dependence of the birefringence is well correlated with the structural changes as predicted by the theoretical model. The model parameters obtained and the existence of a thermal hysteresis of about 0.5 K demonstrate the first-order character of the phase transition.

1. Introduction

In potassium thiocyanate (KSCN) an improper ferroelastic phase transition takes place at $T_{tr} = 415.3$ K, where the high-temperature tetragonal phase D_{4h}^{18} (I4/mcm) transforms into the low-temperature orthorhombic structure D_{2h}^{11} (P*b*cm) (Wrzewnewsky 1912, Yamada and Watanabe 1963). The volume of the unit cell is doubled at the transition. A recent structural study of KSCN (Yamamoto *et al* 1987) confirmed the role of the SCN^- rod-like ion orientational ordering in the transition mechanism, in agreement with the observed value of the transition entropy close to $R \ln 2$ (Sakiyama *et al* 1963). Spontaneous displacement of the potassium ions, well correlated with the SCN^- ordering, was also detected (Yamamoto *et al* 1987). A pseudospin model involving the volume-dependent interaction energy was applied to describe the previous structural data (Yamada and Watanabe 1963).

The measurement of the birefringence can give accurate information on the temperature dependence of the order parameter. Simple symmetry considerations yield a connection between the particular birefringence and the order parameter (Fousek and Petzelt 1979). In KSCN, the spontaneous part (i.e. the part induced by the phase transition) of any birefringence $\Delta_s n_{ij}$ can be expressed as

$$\Delta_s n_{ij} = C_{ij}\eta^2 + C'_{ij}\eta^4 + \ldots \qquad (1)$$

where, at least close to T_{tr}, the first term is expected to prevail.

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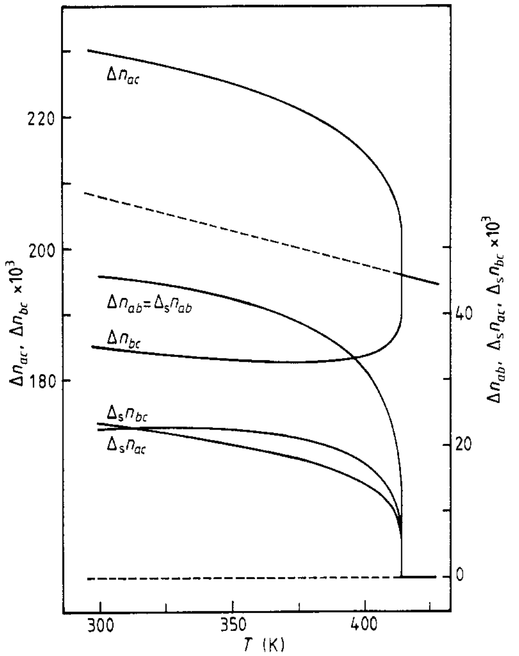

Figure 1. Birefringence of KSCN.

2. Experimental details

Single crystals of KSCN were grown from an acetone solution (Fuith *et al* 1989). 0.05–0.3 mm thick plates perpendicular to the crystallographic axes and optically polished were used for this study. Birefringence was measured with a He–Ne laser by a simple analogue system employing the error signal from a lock-in detector to drive the Babinet–Soleil compensator. With electro-optic modulation, the sensitivity was better than 10^{-6}. The sample temperature was changed continuously with a rate of $1\ \mathrm{K\ min^{-1}}$ or $0.1\ \mathrm{K\ min^{-1}}$ in the transition region. Because ferroelastic domains commonly appear when the samples are cooled from the high-temperature phase (Schranz *et al* 1988), only the data from the first heating runs were taken. In figure 1 the temperature dependences of Δn_{bc}, Δn_{ac} and Δn_{ab} are plotted. Among them the Δn_{ab} is the morphic birefringence, being equal to zero in the tetragonal phase above T_{tr}, and therefore $\Delta_s n_{ab} = \Delta n_{ab}$ holds. On the other hand, the magnitudes of Δn_{bc} and Δn_{ac} are fairly large. They were determined at room temperature using an Ehringhaus compensator within the polarising microscope. Due to the strong dispersion, an error in the resulting absolute values of several per cent is possible. To obtain the spontaneous parts $\Delta_s n_{bc}$ and $\Delta_s n_{ac}$, which are also included in the figure, a baseline obtained by the linear extrapolation of the high-temperature data has been subtracted as usual. In figure 2 the spontaneous parts of the three Δn_{ij} are shown normalised at 413 K. It is seen that in agreement with the theoretical predictions their temperature dependences are practically the same near T_{tr}. The differences at lower temperatures probably result from the different contribution of the higher-order terms in equation (1), but also an error of the extrapolated baseline could be, in principle, partly responsible for it. Our results correlate very well with the structural data (Yamamoto *et al* 1987), as can be seen in figure 2. Here, both the SCN^- ordering and the K^+ displacement data are included (squared, because $\Delta n \simeq \eta^2$) for

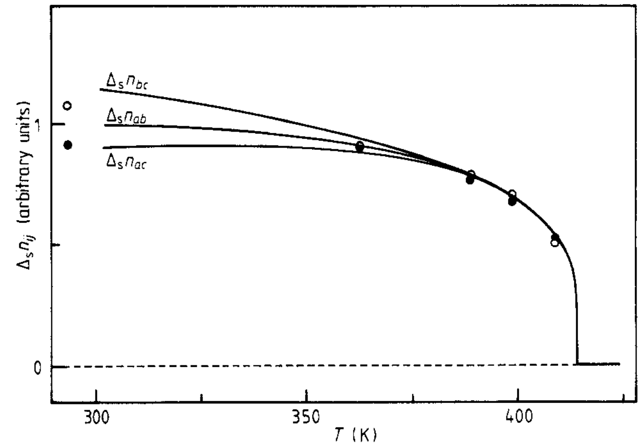

Figure 2. Spontaneous birefringences in KSCN, scaled in the transition region (full curves) and the structural data after Yamamoto *et al* (1987). Full circles: SCN^- ordering; open circles: K^+ displacement in the *a* direction.

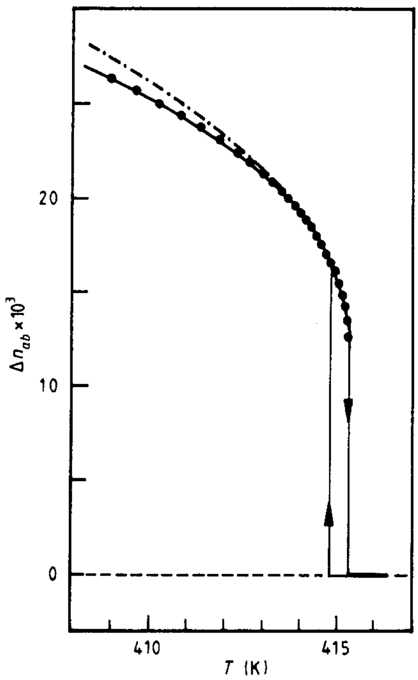

Figure 3. Birefringence $\Delta_s n_{ab} = \Delta n_{ab}$ in the transition region (dots). Full and chain curves are the best fits according to the pseudospin model and Landau theory, respectively.

comparison. The birefringence measurements, however, provide more detailed information in the region of the phase transition. In figure 3 the behaviour of $\Delta_s n_{ab} = \Delta n_{ab}$ near T_{tr} is shown. An apparent jump in the birefringence and the thermal hysteresis of T_{cr} of about 0.5 K demonstrates the first-order character of the transition.

Table 1. Model parameters.

	A	T_c	$T_{tr} - T_c$
$\Delta_s n_{bc}$	0.48 ± 0.04	412.4	2.9
$\Delta_s n_{ac}$	0.53 ± 0.04	410.7	4.6
$\Delta_s n_{ab} = \Delta n_{ab}$	0.50 ± 0.02	411.8	3.5

3. Discussion

Theoretical models of the order–disorder phase transition in KSCN were suggested by Yamada and Watanabe (1963) and by Schranz *et al* (1988, 1989). A compressible Ising system with volume-dependent spin–spin interaction constant is considered, each spin representing a SCN^- ion in a particular orientation. The static behaviours of the two models are the same, giving the temperature dependence of the order parameter η by an implicit function

$$\eta = \tanh[(T_c/T)\eta + (T_c/T)A\eta^3] \qquad (2)$$

where T_c and A are constants. The magnitude of A determines the character of the $\eta(T)$ dependence, which is continuous for $A < \frac{1}{3}$ but discontinuous for $A > \frac{1}{3}$. In the latter case the first-order phase transition occurs at $T_{tr} > T_c$. Yamada and Watanabe, supposing a second-order phase transition, have found $A < \frac{1}{3}$ from the structural data. We also tried to fit our $\Delta_s n_{ij}$ curves by taking $\Delta n_{ij} = C_{ij}\eta^2$ and using equation (2). We obtained very reasonable fits (figure 3) in a wide temperature range between T_{tr} and $T_{tr} - 70$ K (see also Kroupa *et al* 1988). The resulting model parameters are shown in table 1. The scatter of the parameters does not seem to be significant; it may be connected with contingent experimental errors in the region of the very high slope of $\Delta n(T)$ close to T_{tr}. The mean values of the parameters are close to values for the morphic birefringence Δn_{ab}, for which also the accuracy of the measured data was the best and the misfit parameter was the smallest (figure 3). The magnitude of $A = 0.5$ confirms the first-order character of the transition. We also tried to fit our data using Landau theory for a first-order phase transition. With terms up to the sixth order in the thermodynamic potential, only a narrow region below T_c is described properly (figure 3). For the critical temperature T_c, however, the fit again gives $T_c = 412$ K.

4. Conclusions

In KSCN, the temperature dependence of the birefringence is well correlated with the structural changes, in agreement with the theoretical predictions. Accurate birefringence measurements then confirm that the phase transition can be well described using the Ising model with volume-dependent interaction constants. The model parameters obtained are consistent with a discontinuous character of the phase transition.

Acknowledgments

This work was carried out under project No P6758P of the 'Österreichische Fond zur Förderung der wissenschaftlichen Forschung'. T Streuselberger's contribution to the growth of the crystals is gratefully acknowledged.

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