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1994 J. Phys.: Condens. Matter 6 3469

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# Domain formation in the order–disorder phase transition of RbSCN

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Received 24 December 1993, in final form 4 February 1994

**Abstract.** The order–disorder phase transition in RbSCN connected with a head–tail re-orientation of the linear SCN molecule is investigated by diffuse neutron scattering techniques. The experiment corroborates earlier findings in the isostructural compound KSCN showing that disordering occurs by the increased formation of antiphase domain boundaries whereas within the bulk of the domains the SCN molecules remain locally in an ordered configuration even at temperatures near the melting point. A comparison with KSCN indicates that the strong asymmetry of the critical behaviour with respect to  $T_c$  is caused by the influence of elastic interactions on the domain morphology

## 1. Introduction

The formation of domain patterns during phase transitions is an important topic of the current literature [1–3]. The evolution of the domain characteristics—i.e. their size and shape and the behaviour of domain boundaries—is investigated in different systems under various non-equilibrium conditions by both experiments and computer simulations. Recently, the domain formation during order–disorder phase transitions has attracted new interest—especially in connection with oxygen ordering in high- $T_c$  compounds [4, 5].

Some molecular crystals of the RSCN family ( $R = K, Rb, \dots$ ) show an order–disorder phase transformation related to the re-orientation of the linear SCN molecules. This re-orientation is connected to a structural change from an orthorhombic phase (figure 1(a)) to a tetragonal structure (figure 1(b)) at higher temperatures. In the orthorhombic phase the SCN molecules are in an ordered antiferroelastic configuration. At higher temperatures a disordering of the head–tail arrangement of the SCN molecules occurs and the structure becomes tetragonal [6, 7].

A recent elastic neutron scattering investigation of the order–disorder transition in KSCN revealed the formation of microdomains connected with the phase transformation [8]. Evidence for the domains was given by diffuse scattering intensities observed near superlattice points characterizing the ordered low-temperature phase. The diffuse intensities indicate that in the core of all domains the SCN molecules are within an ordered configuration whereas they are disordered at the antiphase boundaries between domains. However, below and above  $T_c$  the domain patterns are quite different. Below  $T_c$  ordered domains with a typical size of 25 Å are embedded within a long-range-ordered matrix. These domains of finite size are enclosed by antiphase boundaries. With increasing temperature the density of the domains increases but their size remains constant.

On the other hand, above  $T_c$ , no long-range order exists and the short-range order observed can be described by an ensemble of ordered microdomains separated by a

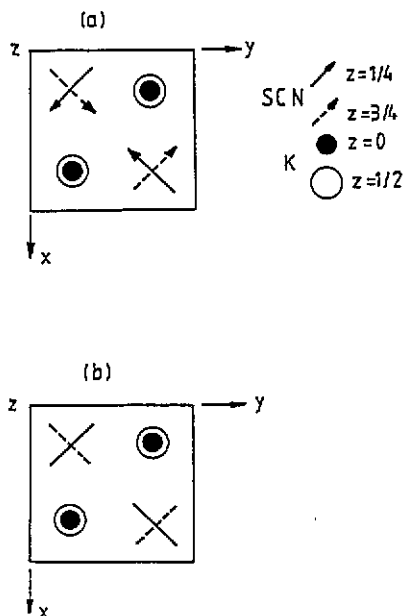


Figure 1. (a) Structure of the orthorhombic low-temperature phase of RbSCN. At room temperature the lattice parameters are [6]  $a_0=6.842 \text{ \AA}$ ,  $b_0=6.896 \text{ \AA}$ ,  $c_0=8.017 \text{ \AA}$ . (b) Structure of the tetragonal high-temperature phase of RbSCN. The lattice parameters are  $a_1=6.948 \text{ \AA}$ ,  $c_1=8.264 \text{ \AA}$ .

percolated network of antiphase boundaries. With decreasing temperature the mean size of the domains increases and shows a divergent behaviour when approaching  $T_c$  from above. Moreover, from an evaluation of the integral diffuse intensity it was found that in the 'disordered state' above  $T_c$  most of the SCN molecules remain within a locally ordered arrangement. In other words, above  $T_c$  the increasing disorder is essentially confined to the total interface of the domain system whereas the bulk of the microdomains exhibits an ordered SCN configuration. Furthermore, it was noticed that the shape of the domains is anisotropic in space with a constant anisotropy ratio in the entire temperature range from  $T_c$  up to the melting point of the system.

In order to obtain a more general insight into these peculiar features of domain formation connected with order-disorder transitions in molecular crystals we performed an additional neutron scattering experiment on RbSCN.

RbSCN shows a similar orthorhombic-tetragonal phase transition related to a similar re-orientation of the linear SCN molecule but, on the other hand, has different structural characteristics e.g. a stronger orthorhombicity, a greater  $c/a$  ratio and also a larger unit cell volume. Moreover, the phase transition occurs at higher temperature—i.e. near  $162 \text{ }^\circ\text{C}$  instead of  $142 \text{ }^\circ\text{C}$  in KSCN [6]. Furthermore, despite the fact that in RbSCN the elastic constants are still unknown, it may safely be conjectured that the heavier RbSCN compound with a greater unit cell volume has generally softer elastic properties than KSCN.

The different structural and elastic properties influence the domain patterns during the phase transition and the present experiment may help to elucidate its peculiar features, in particular the strong asymmetry of the critical behaviour observed with respect to  $T_c$ .

## 2. Experimental details

The neutron scattering measurements were done on the triple-axis spectrometer VALSE located at a cold neutron guide position of the Laboratoire Léon Brillouin at Saclay.

The incident neutron energy was  $14.7 \text{ meV}$ . Pyrolytic graphite PG(002) crystals were used as monochromator and analyser, respectively. The collimations were  $30'$ . A PG filter

was put into the incident beam in order to eliminate higher-order contaminations.

Single crystals of RbSCN with a mosaic width smaller than  $20'$  were investigated. The spectrometer was operated in the elastic mode. The diffuse scattering investigations were performed from room temperature up to  $183\text{ }^{\circ}\text{C}$ .

### 3. Scattering results

The measurements were started by an investigation of the neighbourhood of the (100) point in the ( $a$ ,  $c$ ) plane of the reciprocal lattice of the orthorhombic phase. The (100) point is a superlattice point related to the antiferroelastic configuration of the SCN molecules in the ordered phase.

At room temperature a sharp Bragg reflection above a flat background was observed. The Bragg intensity was in accordance with calculated intensities of the orthorhombic structure. After heating to  $130\text{ }^{\circ}\text{C}$  a broad diffuse intensity distribution appeared at the bottom of the (100) superlattice reflection (figure 2). Further heating to  $157\text{ }^{\circ}\text{C}$  and then to  $161\text{ }^{\circ}\text{C}$  induced an intensity increase but the width of the diffuse intensity distribution essentially remained constant. It should be noticed that at  $161\text{ }^{\circ}\text{C}$  the system is just below the critical temperature of  $162\text{ }^{\circ}\text{C}$ .

The diffuse intensity distribution could be well fitted by a Gaussian. In scans along the [100] direction the position of the centre of the Gaussian was not identical to the position of the (100) Bragg peak but was shifted somewhat towards higher  $Q$ -values (figure 2). A shift of similar size of the Gaussian diffuse intensity distribution was likewise observed at the (300) superlattice reflection. On the other hand no diffuse intensity was found near the (200) fundamental reflection.

During heating from room temperature up to  $160\text{ }^{\circ}\text{C}$  the intensity of the (100) superlattice reflection decreased (figure 3). The intensity decrease roughly corresponds to the intensity increase of the diffuse scattering.

Moreover, as in KSCN, a Huang-type scattering was observed near (002) and (004) fundamental reflections at about the temperature where the Gaussian intensity distribution appeared near the superlattice points (figure 4). The scattering near (002) and (004) points has the classical characteristic of distortion scattering i.e. its intensity increases as  $Q^2$  and is asymmetric with respect to the Bragg point. From the asymmetry observed—i.e. the stronger intensity at higher  $Q$ -values—it follows that the distortion is caused by dilatational strains of the lattice [9].

At the critical temperature the sharp superlattice reflection completely disappeared and a Lorentzian intensity distribution was observed (figure 5). On further heating the peak intensity of the Lorentzian decreased but even a few degrees below the melting temperature a considerable diffuse intensity was still present near the superlattice point. A Lorentzian fit to the data gave a temperature dependence of the widths along [100] and [00 $l$ ] which is shown in figure 6. The values in figure 6 show an anisotropy for the widths in reciprocal space: the width of the distribution along the  $a$ -direction—i.e. [100]—is smaller by a factor of about 1.36 than that along the  $c$ -direction—i.e. (10 $l$ ) (in KSCN the anisotropy factor was near 1.6). Furthermore, despite the fact that the peak intensity diminishes with increasing temperature figure 7 shows that the integrated intensity of the Lorentzian essentially remains constant for the entire temperature range above  $T_c$  (the integration is carried out over the two dimensions of the scattering plane).

It should be noticed that above  $T_c$  the distortion scattering near the (002) and (004) points disappeared.

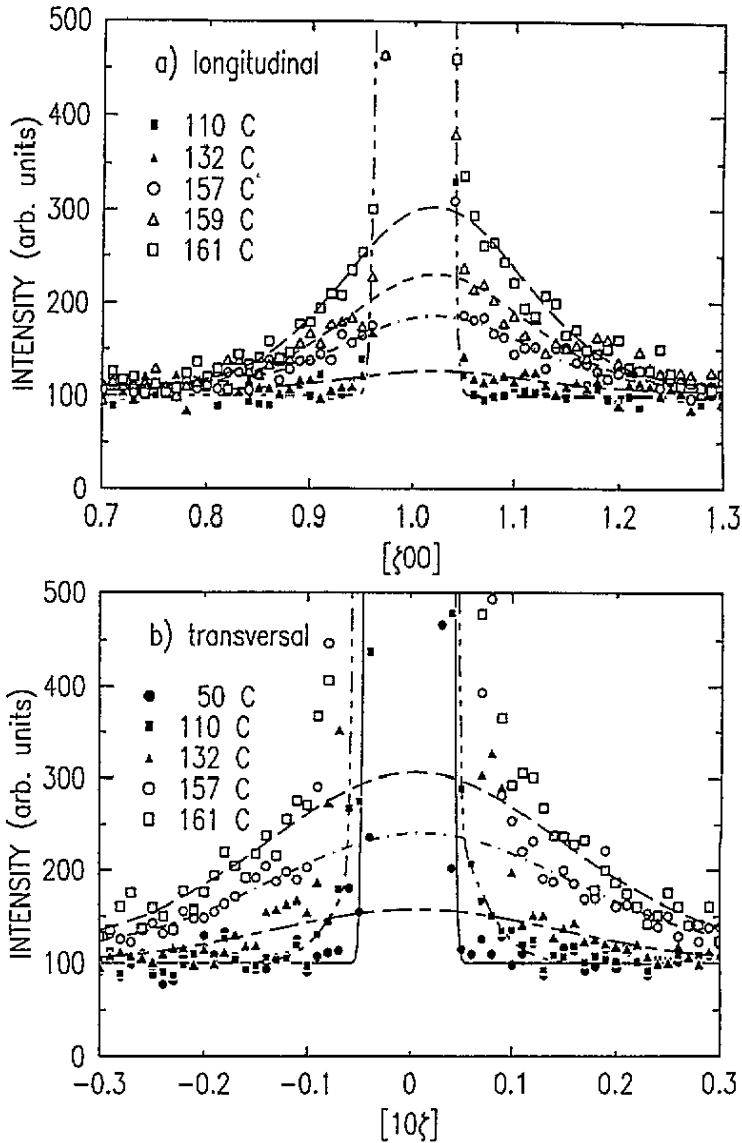


Figure 2. Diffuse intensity distributions near the (100) superlattice point: (a) in longitudinal scans along the [100] direction at different temperatures below  $T_c$ ; (b) in transverse scans along (10). The lines represent Gaussian fits to the diffuse intensity distributions.

#### 4. Discussion

The present experiment has confirmed characteristic features connected with the order-disorder phase transition in RbSCN. The results corroborate earlier findings obtained in KSCN.

Above  $T_c$ , a Lorentzian intensity distribution is found near the (100) superlattice point. This intensity distribution broadens with increasing temperature. The most remarkable result is the observation that the integrated intensity of the Lorentzian remains constant up

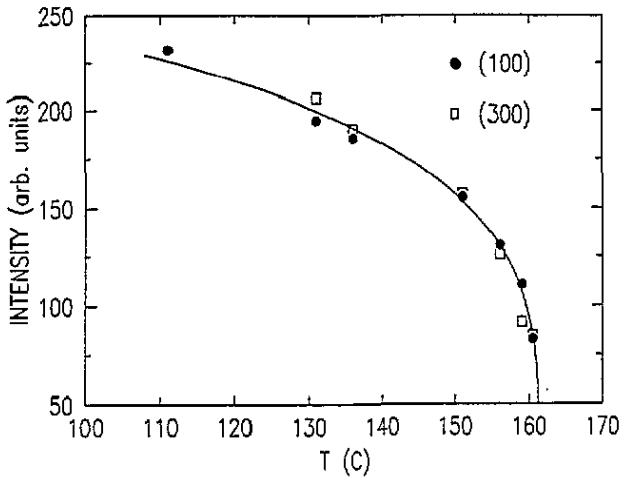


Figure 3. Temperature dependence of (100) and (300) superlattice reflections drawn on the same scale. The line represents a fit of the relation  $I \sim (T_c - T)^{2\beta}$  to the data yielding  $\beta = \frac{1}{8}$ .

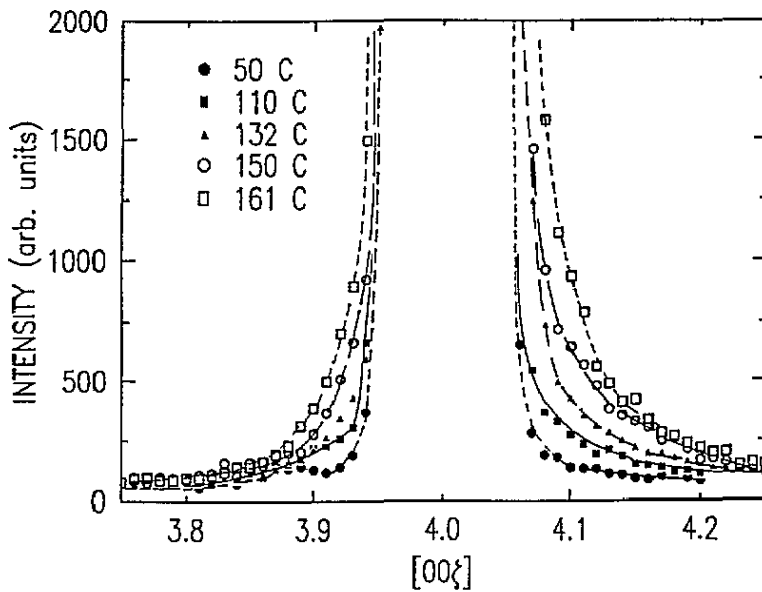
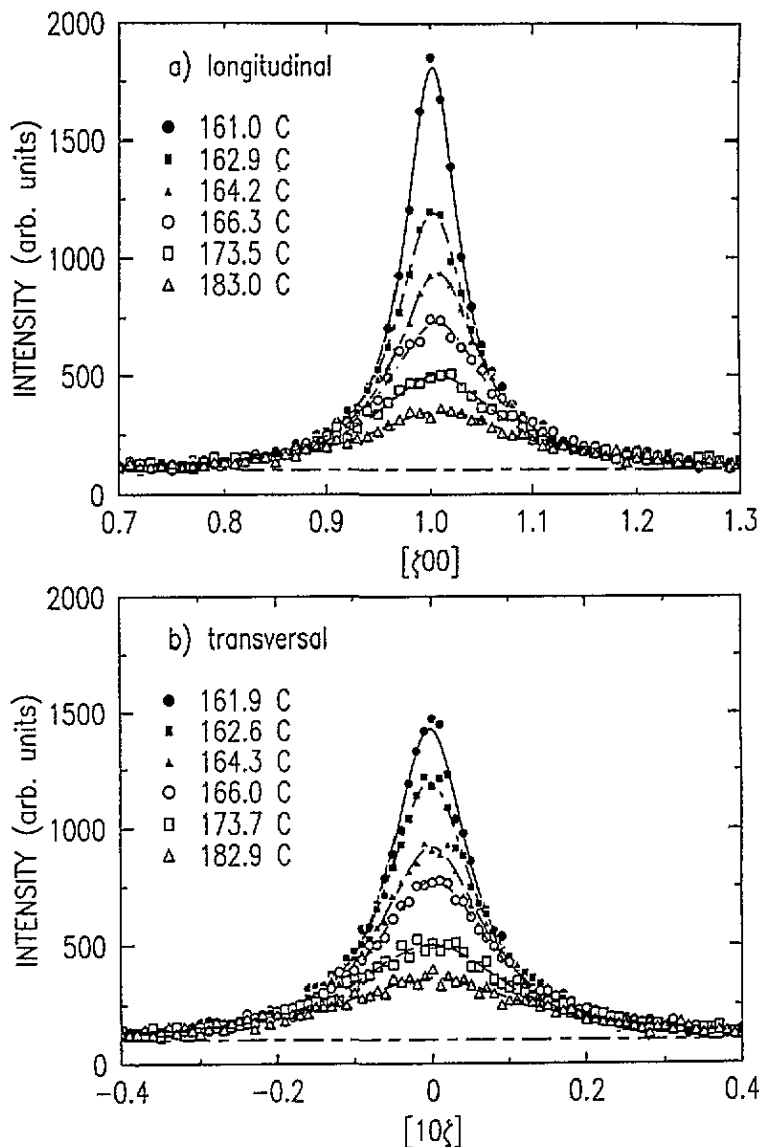


Figure 4. Diffuse elastic scattering appearing near the (004) fundamental reflection along [001] (*c*-direction). The lines are guides to the eyes.

to temperatures near the melting point.

Diffuse intensities near superlattice points are induced by SCN molecules within an ordered local arrangement. This means that in RbSCN the SCN molecules never become randomly oriented on a local scale despite the fact that the long-range order has disappeared. From the constant integrated intensity, from temperatures just above  $T_c$  to temperatures near the melting point, it follows that most of the SCN molecules remain within an ordered local configuration. If the local SCN configurations are described by ordered domains then the structural state above  $T_c$  may be seen as an ensemble of domains separated by antiphase



**Figure 5.** Diffuse intensity distributions observed above  $T_c$  near the (100) reciprocal lattice point (a) in scans along [100], (b) in scans along [10 $\xi$ ]. The full lines represent Lorentzian fits to the data. The dash-dotted line shows the background in the ordered phase.

boundaries. In such an arrangement most of the SCN molecules contribute to the short-range order scattering observed near superlattice points. Its integral intensity is then given by the total volume of the ordered domains. On the other hand, the SCN molecules within a disordered configuration are confined to the domain boundaries and their number is related to the total domain interface.

With increasing temperature the domain boundary density increases and consequently the mean domain size decreases inducing the broadening of the diffuse intensity distribution observed. The integral short-range order intensity, however, is still proportional to the

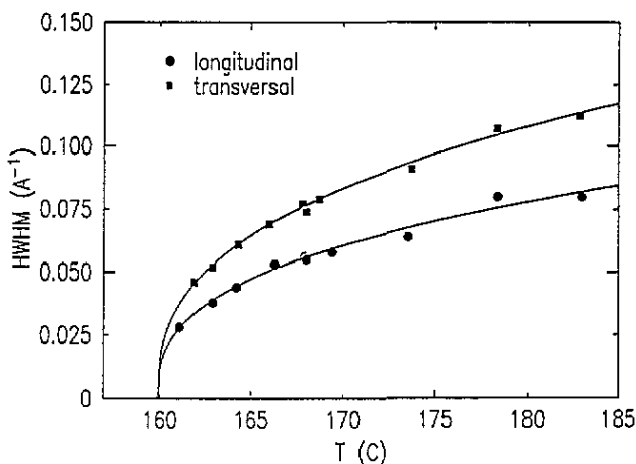


Figure 6. The halfwidths (HWHM) of the Lorentzian intensity distributions along [100] (longitudinal) and [10 $\bar{l}$ ] (transverse) directions as functions of temperature.

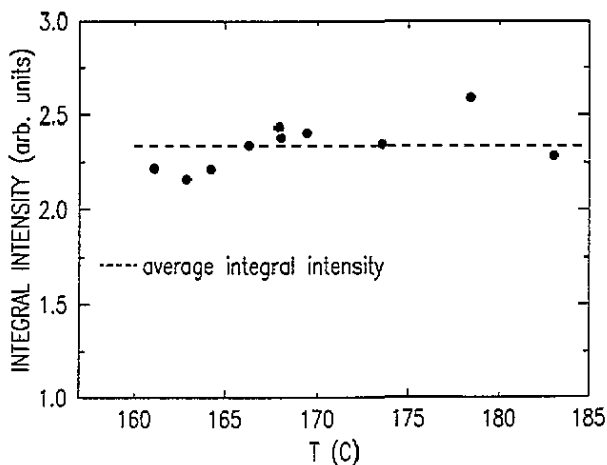


Figure 7. Evaluated integral intensities of the intensity distributions observed near the (100) reciprocal lattice point. The integral intensity is given by the peak intensity multiplied by the widths measured along [100] and [10 $\bar{l}$ ].

total domain volume and consequently remains nearly unchanged in agreement with the experimental observation.

On the other hand, below  $T_c$  the experiment reveals quite different features. About 30 °C below the transition temperature a Gaussian diffuse intensity distribution is found at the bottom of the sharp superlattice reflection. With increasing temperature the intensity increases but the width of the distribution remains constant. The broad diffuse scattering distribution at the bottom of a superlattice reflection indicates the presence of ordered antiphase domains embedded within the long-range-ordered matrix. From the width of the diffuse distribution a value of about 30 Å is obtained for the mean size of the antiphase domains. This size remains unchanged up to temperatures close to the transition temperature and consequently below  $T_c$  no divergence of the mean domain size is observed.

Therefore, a first comparison of the experimental observations above and below  $T_c$ ,



reveals a strongly asymmetric domain behaviour with respect to the transition temperature. In order to show this asymmetry we have plotted the mean domain size as obtained from the measured widths of the intensity distributions versus the entire temperature range of this experiment (figure 8). The figure clearly shows that below  $T_c$  the size of the domains is stabilized whereas above  $T_c$  a divergent behaviour extending over a rather large temperature range is found.

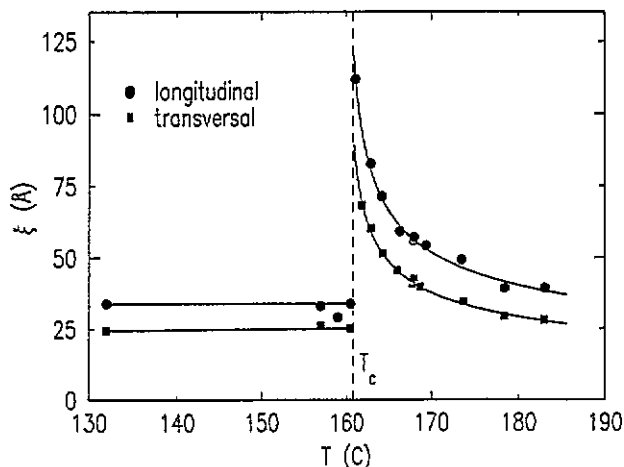


Figure 8. The average size of antiphase domains observed in the entire temperature range investigated above and below  $T_c$ .

Furthermore, the present experiment has shown that a distortion scattering appears at temperatures below  $T_c$  where simultaneously antiphase domains of constant size are observed. The distortion scattering increases together with the number of antiphase domains but disappears above the transition temperature. It is therefore reasonable to ascribe the observed distortion to the formation of antiphase domains of finite size within the long-range-ordered matrix. Indeed, if it is assumed that the lattice parameter within the domain boundary region is somewhat different from the lattice parameter within the bulk of the ordered lattice, then a domain of finite size creates a lattice distortion in the system [10].

On the other hand, above  $T_c$  the distortion scattering has disappeared. This means that the domain structure above the transition temperature is essentially determined by the domain boundary energy. The experiment has shown that the diffuse scattering distribution is anisotropic—with a constant ratio of the widths along the  $c$  and  $a$  directions respectively—over the entire temperature range above  $T_c$ . The corresponding anisotropic mean domain shape can therefore be related to an anisotropic surface energy generally present in molecular systems.

The scattering features found in RbSCN are qualitatively similar to those previously observed in the isostructural KSCN compound. This means that in both systems the phase transition occurs qualitatively in a similar way. However, two characteristics of the domain pattern show significant differences. First, in RbSCN the anisotropy in the domain shape above  $T_c$  is less pronounced. Second, in RbSCN the domains of finite size observed below  $T_c$  are somewhat larger.

If the anisotropy in the shape of the domains above  $T_c$  is related to the anisotropy of the surface energy then RbSCN represents the less anisotropic system. The observation that the surface energy becomes more isotropic when the potassium ion is replaced by

the heavier rubidium ion may be related to the fact that the substitution of Rb induces an increase of the  $c/a$  ratio of the orthorhombic (tetragonal) structure which is then closer to a hypothetical cubic configuration where the  $c$ -axis becomes a cubic [002] direction and the  $a$ -axis a cubic [110] direction. Within the class of alkali-SCN compounds the cubic structure is finally realized with the large Cs ion—i.e. in CsSCN—where in terms of a tetragonal crystallographic notation  $c/a = [002]/[110] = \sqrt{2}$ .

Moreover, in RbSCN the domains of finite size below  $T_c$  are somewhat larger than previously found in KSCN. In this regime distortion scattering is observed and therefore the domains of finite size with closed antiphase boundaries induce a lattice distortion. This lattice distortion increases with the density of the antiphase domains as experimentally observed. Likewise, the lattice distortion and the elastic energy connected therewith may also increase with the size of the domains. It is therefore a reasonable outcome of the present experiment that in the softer RbSCN lattice the closed domains are larger than those in the harder KSCN compound. It may follow that the elastic energy stabilizes the domain size below  $T_c$  and is responsible for the lack of divergent behaviour.

Furthermore, we observed that the maxima of the Gaussian intensity distributions are shifted towards higher  $Q$ -values near the (100) and (300) superlattice reflections. For the two regions in reciprocal space the shift is similar in size and consequently is not related to a different lattice parameter within the small domains. The shift, however, can rather well be reproduced by a calculation assuming that the interface between a small antiphase domain and the matrix has a lattice spacing increased by a few per cent with respect to the bulk of the material. Experimentally, the shift is observed along the [100] direction and the scattering features can be simulated by the following simple expressions.

For an ordered system consisting of A and B planes with scattering powers  $f_A$  and  $f_B$ , respectively, the scattering amplitude  $A(Q)$  is given by

$$A(Q) = \sum_n (f_A e^{iQna} + f_B e^{iQ(n+1)a}) \quad (1)$$

where  $a$  is the lattice constant.

If now an antiphase domain of size  $2ma$  is added, then the scattering amplitude of the new system  $B(Q)$  is written

$$B(Q) = A(Q) + e^{iQd} \sum_{k=0}^m (f_B e^{iQka} + f_A e^{iQ(k+1)a}) \quad (2)$$

where  $d$  is the lattice spacing at the domain boundary and the ratio  $d/a$  is a measure of the lattice distortion at the domain interface.

In the calculations antiphase domains were randomly inserted in the long-range-ordered matrix. The calculated intensity distribution for  $d/a = 1.04$  is shown in figure 9 together with the experimental data. If the  $d/a$  ratio is taken smaller than unity then an intensity shift to smaller  $Q$ -values is observed.

Therefore, the small shift in the diffuse intensity distribution is also an indication that the lattice distortion observed takes its origin at the antiphase domain boundary.

In summary, the present experiment on RbSCN has revealed qualitatively similar features of domain pattern formation connected with the order-disorder transition of the linear SCN molecule to those previously described in KSCN. In both systems above  $T_c$  most of the SCN molecules remain within a locally ordered arrangement whereas the long-range order has disappeared. The disorder is essentially confined to the domain boundaries whose density increases with temperature. The comparison of the two systems shows that the peculiar asymmetric domain behaviour with respect to  $T_c$  is due to the influence of

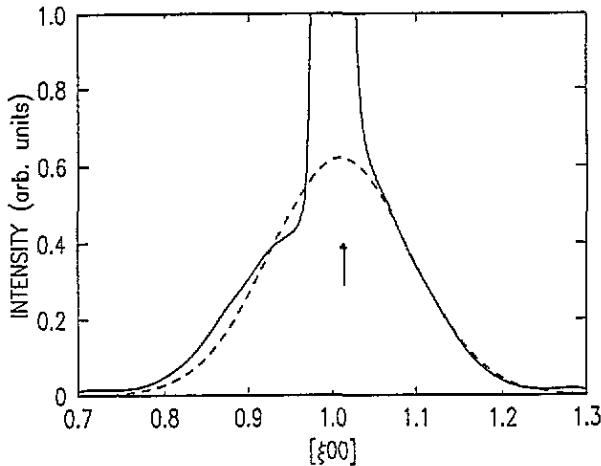


Figure 9. Calculated intensity distribution near the (100) reciprocal lattice point along the [100] direction produced by an ensemble of antiphase domains with a typical size of eight lattice spacings embedded within a long-range-ordered matrix. It is assumed that the lattice constant is increased at the interface to the matrix by about 4% with respect to the bulk. The calculated diffuse intensity distribution is shifted somewhat towards higher  $Q$ -values as is observed in the experiment (figure 2(a)).

elastic interactions on the domain morphology inhibiting a critical divergence of the mean domain size below  $T_c$ .

### Acknowledgments

Our work was partly supported by the Fonds zur Förderung der wissenschaftlichen Forschung in Austria.

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