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Neutron diffraction study of the lattice distortion related to charge ordering in $Sr_{14}Cu_{24}O_{41}$

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Using elastic neutron scattering on a triple axis spectrometer we have studied the temperature dependence of the crystal structure in $Sr_{14}Cu_{24}O_{41}$ across the range where charge ordering phenomena are expected. Several superstructure reflections are observed at low temperature which fully disappear above ~200 K. Most of these reflections can be explained by a modulation of both the chain and the ladder-lattices due to the charge ordering. However, the peak position as well as some weaker reflections point to a close connection between the charge ordering and the modulations of the incommensurate composite structure.

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The spin-ladders compounds with formula $Sr_{14}Cu_{24}O_{41}$ or related exhibit a rather complex crystallographic structure due to their composite character.[1] The materials consist of an alternating stacking of two distinct types of layers. One is formed by $Sr_2Cu_2O_3$ with a ladder-like structure and the other contains CuO_2 chains.[2,3] The incommensurate modulation results from the misfit between the lattice parameters of these plane elements. Whereas the a parameter, $a \sim 11.47$ Å, is the same in both sublattices due to the free arrangement of the two CuO_2 chains, the c parameters reflect the different Cu–O–Cu bonding, 180° and 90° in ladders and chains, respectively, and roughly differ by a factor of $\sqrt{2}$, $c_l=3.95$ and $c_c=2.75$ Å. The b parameter corresponding to the stacking is the same for both elements. The reciprocal space can thus be described by a superposition of two lattices with identical $a^*=2\pi/a$ and $b^*=2\pi/b$ parameters, but two different $c^*=2\pi/c_i$ parameters. In a four-dimensional notation, each reflection $(hklm)$ can be identified with the reciprocal wave vector $h\cdot a^*+k\cdot b^*+l\cdot c_c^*+m\cdot c_l^*$ where the indices l and c denote the ladder and chain subsystems, respectively. Reflections with neither the l nor the m components nonzero are common to both lattices, those with just one of them nonzero can be attributed to one lattice, and those with both nonzero result from an intermodulation of both lattices and are called satellites. Alternatively, one may use a three-dimensional notation with noninteger indexes. Throughout the paper we use the chain-c_c parameter as reference for the misfit direction in three-dimensional notation. The composite structure of $Sr_{14}Cu_{24}O_{41}$ or similar compounds has been studied by several groups finding sizeable modulation of both lattices.[4–6]

Several quite distinct studies find strong evidence for an additional distortion of the crystal structure at low temperature. NMR experiments by Takigawa *et al.*[7] indicate that the single Cu-chain site at room temperature splits into two distinct sites below about 200 K. At this temperature also transport properties exhibit strong anomalies[8,9] suggesting that the transition is related to charge localization. Finally, the analysis of the magnetic excitation spectra by inelastic neutron scattering indicates the formation of isolated dimers.[13–16] From the exact formula, $Sr_{14}Cu_{24}O_{41}$, one calculates six holes per formula unit, which, when situated in the chain system, yield a 6:4 ratio between formally Cu^{3+} and Cu^{2+}. X-ray absorption measurements, however, indicate that not all of the holes are situated in the chain system.[12] A hole around Cu^{3+} forms a Zhang-Rice singlet[8] separating the remaining Cu^{2+} spins. Denoting the singlet sites by 0 and the magnetic sites by ↑ or ↓, one may describe the magnetic arrangement by

$$\uparrow 0 \downarrow 00 \uparrow 0 \downarrow 00 \uparrow 0 \downarrow 00 \cdots,$$

(model I) which corresponds to dimers of two spins coupled across one hole; neighboring dimers are separated by two successive holes. Such an arrangement will give rise to quintupling of the chain c_c parameter or a modulation with $q=(0,0,0.2)$. Alternatively, in model II, it has been proposed that there is a modulation of type

$$\uparrow 0 \downarrow 0 \uparrow 0 \downarrow 0 \uparrow 0 \downarrow 0 \uparrow \cdots,$$

i.e., alternating occupation by spins and singlets, which requires an additional spin-Peierls-like distortion in order to explain the observed dimerization. This model yields a quadrupling of the c parameter or a modulation with $q=(0,0,0.25)$. Several groups have discussed their results in these models.[7,13–17]

The low temperature transition has been studied by different diffraction techniques. Using x rays of moderate energy Cox *et al.*[18] found an appearance of additional reflections at low temperature which may be indexed in the fourfold lattice. On single crystals of the same origin, Fukuda *et al.*,[19] however, found superstructure reflections which can be indexed in the fivefold lattice using hard x rays. In addition, they have shown that the soft x-ray intensity may be altered with a surface treatment. They interpreted their data as evidence for a charge ordering transition with a modulation of $q=(0,0,0.2)$ corresponding to model I and presented a preliminary model for the underlying lattice distortion. van Smaalen comments on this work,[20] arguing that the interpretation of the newly observed reflections is not unambiguous;

they may also be indexed as satellites of the composite structure. In this interpretation, however, one has to accept quite high orders for the satellites and a breaking of the symmetry compared to the normal low-indexed satellites which are stronger and less temperature dependent.

We have studied the charge ordering transition by neutron diffraction and found superstructure reflections similar to the hard x-ray work by Fukuda *et al.*[19] However, in our experiment the reflections disappear completely upon heating to room temperature and exhibit a limited correlation length along the chain direction at low temperature. We propose an interpretation intermediate between those given in Refs. 19 and 20.

A large single crystal of $Sr_{14}Cu_{24}O_{41}$ was cut from a rod obtained with a floating zone mirror furnace;[21] the shape is cylindrical with 5 mm diameter and about 30 mm length. Samples of the same origin were used already in many works.[9–13] The neutron diffraction experiments were performed on the triple axis spectrometer 4F1 of the Laboratoire Léon Brillouin installed at the cold source of the Orphée reactor. This spectrometer operates with a double monochromator and a focusing analyzer, all using the pyrolithic graphite (002) reflection. The sample was mounted in a closed cycle He refrigerator with a temperature stability of 0.5 K in the range 14–300 K. Most scans were performed with a fixed final neutron wave vector of $k_f = 2.662$ Å^{-1} where a pyrolithic graphite filter allows for efficient suppression of the higher order contamination. In most cases we did not mount collimators in the beam which roughly corresponds to an open-33′-50′-50′ collimated configuration. A few additional studies were performed on the thermal four-circle diffractometer 6T2 using a short wavelength of 0.9 Å and a smaller sample.

The large sample exhibits a mosaic spread of about a half degree as determined in high resolution configuration. A specific question concerns the degree of ordering in the chain lattice. Frequently, in composite crystals one may distinguish between the host and the guest lattice. This notation is evident in inclusion composite materials but not in our case. Only the ladder system shows strong bonds in the *a* direction; one may thus consider the chain system as the guest. In doped materials like $Sr_5Ca_9Cu_{24}O_{41}$ or in $La_5Ca_9Cu_{24}O_{41}$ we have found by neutron diffraction that the chain lattice is indeed only poorly defined,[9] in particular the translation symmetry in the *a* direction is not of long range. Figure 1(a) shows the corresponding scan for $Sr_{14}Cu_{24}O_{41}$ demonstrating that the chain order is rather high though not perfect. There is still diffuse scattering in the a^* direction which depends on temperature, see the inset in Fig. 1(a). Upon heating towards room temperature the disorder is significantly enhanced. In contrast to the chain reflections, the same type of scan across the (0 0 0 2) ladder reflection shows a well-defined peak. Also, scans across a strong Bragg peak of the chains in the c^* direction do not show similar tails; instead along this direction the satellites due to the composite character are observed, see Figs. 1(b) and 1(c).

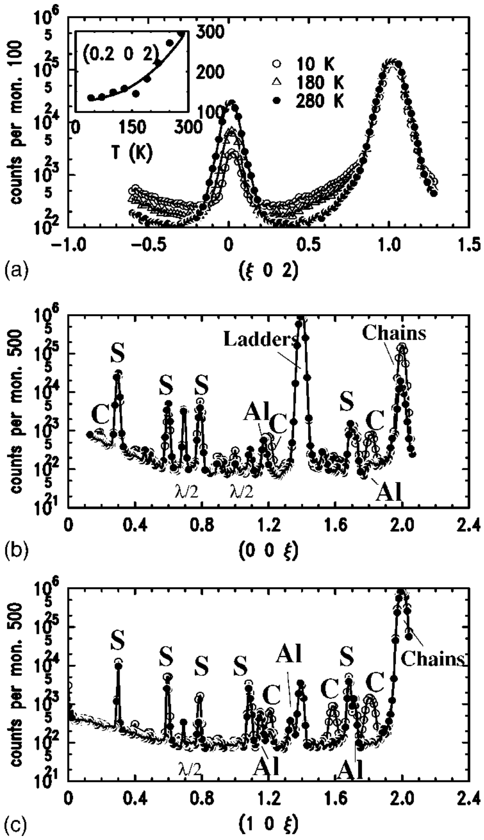

FIG. 1. (a) Scans along the a^* direction across the chain lattice Bragg peaks (1 0 2 0) and (0 0 2 0), note that the latter is weaker and strongly temperature dependent. The inset shows the height of the diffuse scattering at (0.2 0 2) as function of temperature. (b) Scans along the c^* direction across the ladder reflection (0 0 0 2) = (0 0 1.395) and the chain reflection (0 0 2 0) = (0 0 2). (c) Scans along the *c* direction across (1 0 2 0) = (1 0 2). **S** denotes pure satellite reflections, **Al** a contamination by the aluminum sample holder, and **C** a low temperature superstructure peak; $\lambda/2$ denotes a weak contamination through neutrons of half wavelength.

Figure 2 shows the appearance of scattering upon cooling from near room temperature to lowest temperatures. Here it is important to compare pure satellites of the composite lattice with the additional low temperature peaks. For instance, in Fig. 2(a) one sees a typical satellite reflection with little temperature dependence and in particular with a sharp peak profile reflecting the experimental resolution. In Fig. 2(b) too, one finds an ordinary satellite reflection [for example (1 0 1.69)] with little temperature dependence. However, in addition there is the low temperature scattering at (1 0 1.59) and (1 0 1.81). One easily recognizes that this scattering does not show the peak width of the instrumental resolution but is significantly broadened. Figures 2(c)–2(f) show further intensities which are observed at low temperature only. In contrast to Ref. 19, the shown intensities fully disappear above the temperature range, where charge ordering is supposed to occur. The new superstructure peaks are broader than the experimental resolution, down to the lowest temperatures studied. The origin of this broadening is still unclear, it may result from some inhomogeneity either on a macroscopic or a microscopic level. However, the clear difference between the normal satellites and the additional reflections appearing at low temperature points to a different physical origin. The two types of superstructure peaks are also different in their scattering intensities: typical satellite

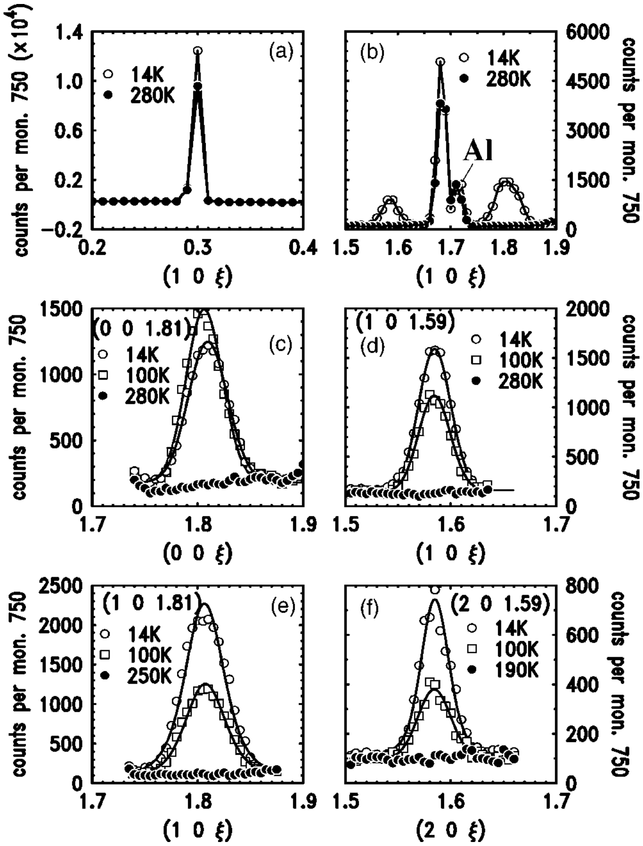

FIG. 2. Scans across satellite and the additional peaks demonstrating their different temperature dependencies and peak widths. (a) Scan across the satellite $(1\ 0\ 0.3) = (1\ 0\ 1\ \bar{1})$ at 14 and 280 K. (b) Scan across the satellite $(1\ 0\ 1.69) = (0\ 0\ 1\ 1)$ at 14 and 280 K; near (1 0 1.59) and (1 0 1.81) new superstructure peaks appear at low temperature which exhibit significant broadening, **Al** indicates an Al contamination. (c) and (d) Scans across the low temperature reflections (0 0 1.81), (1 0 1.59), (1 0 1.81), and (2 0 1.59) at low and high temperatures. Lines denote fits with a Lorentzian peak profile convoluted with the resolution of the triple axis spectrometer.

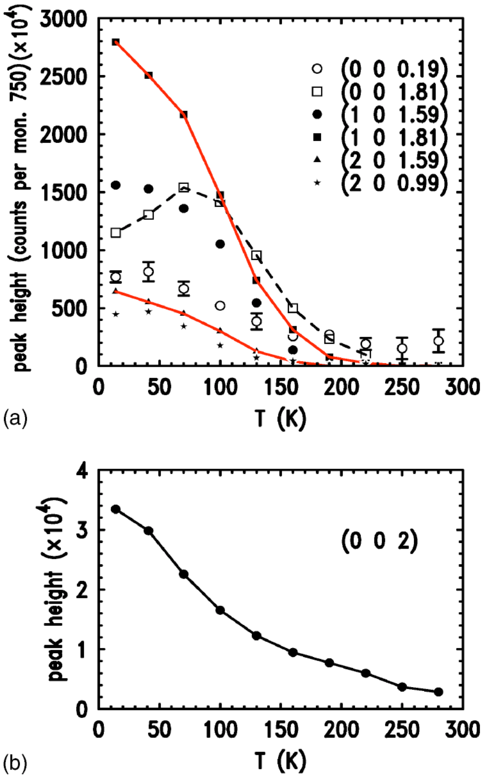

FIG. 3. Temperature dependence of the peak height of the low temperature superstructure peaks obtained by fitting the measured intensity profiles with a convolution of a Lorentzian and the experimental resolution, (a). Part (b) shows the similar temperature dependence of the $(0\ 0\ 2) = (0\ 0\ 2\ 0)$ chain reflection.

reflections are about one order of magnitude stronger than the additional low temperature intensities which are about a factor of 1000 weaker than the strongest fundamental Bragg peaks.

Figure 3(a) presents the temperature dependence of the intensities of the additional reflections. They disappear near 200 K where an anomaly in the electric resistance indicates the onset of charge ordering in crystals of the same origin as the one studied here.[9] We have scanned the complete reachable q_l range for $q_h = 0, 1$, and 2. Therefore we are confident that we get a picture of the main element of the structural change. Our results do not agree well with the x-ray data of Fukuda *et al.*[19] who find sizeable intensity up to room temperature. The fact that the neutron superstructure intensities fully disappear around 200 K suggests a structural phase transition with some symmetry change.

Part (b) of Fig. 3 shows the increase of the intensity of the (0 0 2) chain reflection which is sensitive to the relative shift of the two CuO_2 chains in the chain system, this effect has already been reported in Ref. 15. A similar anomalous intensity increase upon cooling was found in the (0 2 2) and (2 0 2) chain reflections. These temperature dependencies do not agree with a purely structural mechanism, since the strongest increase is found at low temperatures whereas structural changes should level off upon cooling. Instead the (0 0 2) curve resembles the increase of intensity in the low temperature peaks thereby suggesting a common origin. One may further note that the diffuse scattering due to the chain disorder seems to freeze in, in the temperature range where the (0 0 2) and the low temperature peaks increase in intensity.

The position of the additional peaks also does not match precisely with the modulation of (0 0 0.20) reported by Fukuda *et al.*[19] We find the strongest additional peaks at [0 0 0.188(2)], [0 0 1.809(3)], [1 0 1.806(3)], and [1 0 1.585(3)]. The first three reflections may be attributed to a modulation of the chain lattice with a propagation vector of [0 0 0.190(4)], i.e., near to the value reported in Ref. 19. With the experiment using the short wavelength on 6T2 we also observe intensity at (0 0 2.2) which is the opposed modulation induced satellite reflection around (0 0 2). The small but significant difference to the modulation obtained by Fukuda *et al.*[19] may arise from minor differences in the oxygen stoichiometry or just follow a slight difference in the lattice constants, see below. The occurrence of and the nature of the additional reflections seem to be very sensitive to minor differences in composition, since the surface sensitive conventional x-ray study,[18] the hard x-ray experiment,[19] and this neutron study obtain slightly different results.

The almost equally strong reflections at [1 0 1.585(3)] and [2 0 1.585(3)] have to be interpreted in a different manner. The experimental resolution is sufficient to exclude an explanation as second order modulation of the chain lattice, since this would, for example, lead to the position (1 0 1.62). Instead, we interpret that also the ladder system feels the modulation with the same propagation vector, since the ladder reflection (h 0 0 2) corresponds to (h 0 1.395) in three-dimensional notation. Thus the superstructure (h 0 1.585) corresponds to (h 0 0 2)+(0 0 0.19). Again it is important to stress that we also find the opposed satellites at (h 0 0 2) −(0 0 0.19) for $h=0,1$. The modulation of the ladder sublattice has important consequences for its excitation spectrum.[22] So far, the results support the idea of an additional modulation which has the same period on both lattices and which reflects the charge order transition.

In order to extend the Q range studied above the limit attainable with the long wavelength, scans similar to those shown in Fig. 1 were performed on the thermal four-circle diffractometer 6T2, which yields, however, a strongly reduced intensity over background ratio and less Q resolution. Some of the low-temperature peaks, for instance, could not be detected in this configuration due to limited statistics. The short wavelength experiment finds strong peaks appearing at low temperature: (4 0 0.2), (3 0 0.8), (3 0 2.2), (3 0 2.8), and (3 0 3.2) which are well explained with a modulation of about (0 0 0.19). However, there is also evidence that some of the usual satellite reflections exhibit a pronounced temperature dependence, for example $(0\ 1\ 3.6)=(0\ 1\ 5\ \bar{2})$, which seems to disappear above 200 K.

Close inspection of Fig. 3 shows that the temperature dependence of the additional intensities is similar, they all appear below about 200 K. However, their temperature dependence is not exactly identical, as one would expect if they would all reflect the same order parameter. Besides two sharp reflections near (2 0 2.18) which might have some artificial origin, all additional reflections exhibit strong broadening in the c direction. All peaks were fitted by a convolution of a Lorentzian profile with the experimental resolution. The temperature dependence of the obtained half-widths at half maximum which corresponds within Ornstein-Zernicke theory to the inverse of the correlation lengths is given in Fig. 4(a). Again the agreement between the distinct reflections is not perfect; in the average one obtains a correlation length of ~50 Å. Along the a^* direction we obtain a limited correlation length too, which, surprisingly, is larger than the one in the c^* direction, of the order of ~100 Å. The corresponding scan is shown in Fig. 4(b), it indicates some weakly correlated contributions and exhibits a peak at (0.5 0 1.81), which is absent at high temperature. The structural transition around 200 K thus exhibits also some translation symmetry breaking along the a^* direction.

van Smaalen[20] argues that all the additional reflections observed by Fukuda *et al.*[19] can be indexed as composite satellite reflections. This argument gets further support by our results, since the ordering modulation (0 0 0.190) agrees within the error-bars with the $(0\ 0\ \bar{4}\ 6)$ calculated satellite position at (0 0 0.185). This agreement seems not to be a hazard.[23] Since the modulation vector can be indexed by $(0\ 0\ \bar{4}\ 6)$, one may index any modulation of a pure chain or pure ladder reflection as a satellite of the composite structure, eventually in disagreement with the generally expected superspace group.[23]

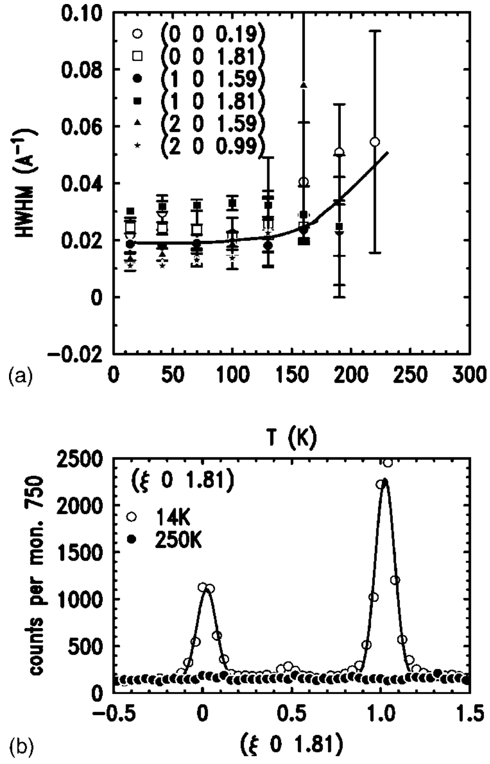

FIG. 4. Temperature dependence of the peak width (half-width at half maximum) of the low temperature superstructure obtained by fitting the measured intensity profiles with a convolution of a Lorentzian and the experimental resolution, (a). Part (b) shows the scans across the (0 0 1.81) and (1 0 1.81) reflections in the a^* direction at 14 and 250 K.

With the triple axis as well as with the four-circle experiments we see further reflections appearing at low temperatures which may not be explained with the (0 0 0.19) modulation of the chain and ladder lattices. With the triple axis spectrometer we find (2 0 0.988), (0 0 0.40), and (1 0 0.40) which are roughly an order of magnitude weaker than the low temperature peaks discussed above. On 6T.2 we observe a strong variation at (0 1 3.6), (0 0 3.6), (2 0 3.6), and other satellite positions of the composite structure. However, we do not observe the (0 0 1.5) reflection reported in Ref. 19. It is worth emphasizing that in our experiment all the intensity appearances or strong variations, which are not already explained with the (0 0 0.19) modulation, occur at q values shifted by (0 0 0.4) from either a ladder or a chain fundamental reflection, i.e., close to the expected second order modulation. The triple-axis experiment, however, allows one to analyze the q position precisely enough to conclude that these three reflections do not exactly correspond to the second order satellites of the $(0\ 0\ 0.19)$ modulation. Instead one may again index them as satellites of the composite structure: $(2\ 0\ 0.988)=(2\ 0\ \bar{6}\ 10)$, $(0\ 0\ 0.40)=(0\ 0\ \bar{1}\ 2)$, and $(1\ 0\ 0.40)=(1\ 0\ \bar{1}\ 2)$; note that the latter two violate the extinction rule given for the modulated structure. The intensities of the reflections (2 0 0.988) and (0 1 3.6) were determined at many temperatures showing a variation very similar to those of the $(0\ 0\ 0.19)$ reflections, see Fig. 3.

The observation of the second order effects again at a position of the composite satellites further supports the interpretation by van Smaalen. However, if one attributes all these additional reflections to ordinary higher order satellites, one may not explain why they disappear with increasing temperature and why this temperature dependence is still quite similar. The modulation of the two sublattices arising from the composite structure has been determined by neutron diffraction as a function of temperature including second order satellite reflections, however, no essential changes have been found[6] between 295 and 7 K. Furthermore, the limited correlation length corresponding to the low temperature reflections remains unexplained in the satellite interpretation. More importantly, there is no simple argument why on one side we observe so many strong reflections with $\Delta q=(0,0,0.19)$ which requires the high order composite satellite indexing $(0\ 0\ \bar{4}\ 6)$ and why on the other side we do not see all the other lower indexed satellites. All this suggests that the new intensities are not ordinary composite satellite reflections but result from the increasing structural distortion reflecting the charge ordering.

We suggest a combined interpretation. The charge ordering or the structural transition evidenced in many experiments[8] seems not to invoke a rigid modulation of the chain and ladders lattices with a rigid period fixed by the charge carriers. Instead this distortion seems to lock into the possible higher order satellites which are related to a highly anharmonic distortion of the composite modulation. The behavior of the charge order induced structural distortion may be compared with a usual charge density wave, which will lock into a commensurate position of the lattice. As the satellite $(0\ 0\ \bar{4}\ 6)$ almost corresponds to the required modulation,[22] the transition can lock into this q value. But still the character of a usual modulation remains present, since the intensities corresponding to that position are dominating. The main additional low temperature scattering is well explained with the modulation character of this ordering, and it appears likely that for most phenomena one may ignore the complication arising from the composite satellite structure and its highly anharmonic modulation. The structural distortion seems furthermore to be associated with a change in superspace symmetry. Although the essential features of the modulated composite structure seem not to change upon cooling,[6] many of the weak satellite reflections exhibit considerable intensity variations, as may be seen by close inspection of Fig. 1. It appears important to recall that the superstructure intensities associated with the charge ordering remain significantly smaller than the strong ordinary satellite reflections.

Depending on the type of radiation used, different aspects of the low temperature superstructure reflections are sensed. With x rays one is more sensitive to the displacements of the heavy cations, whereas neutron diffraction is equally determined by the oxygen positions. Relatively, the x-ray experiment will, therefore, be more sensitive on the satellite aspect and the neutron experiment on the modulation aspect of the low temperature superstructure.

In conclusion, elastic neutron diffraction on a single crystal of $Sr_{14}Cu_{24}O_{41}$ reveals additional reflections appearing upon cooling below 200 K. In this temperature range one also observes an anomalous increase of the $(0\ 0\ 2\ 0)$ reflection[6,15] and freezing of diffuse scattering related to chain disorder. Most of the low temperature superstructure peaks may be well explained by a modulation of both chain and ladder lattices with a common propagation vector $(0\ 0\ 0.19)$. Weaker ones are observed near the positions where second order harmonics are expected. All reflections may be indexed as satellites of the composite structure [for example $(0\ 0\ 0.19)$ corresponds to $(0\ 0\ \bar{4}\ 6)$], but the additional peaks at low temperature differ from the normal satellites due to their strong temperature dependence, due to their weak intensity, and due to their larger width in q space. We interpret these results by a structural modulation associated to the charge ordering locking into the incommensurate composite structure. The charge ordering therefore is associated with a change in the modulations of the two subsystems.

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