Temperature Dependence of the Static Distortion in Incommensurate Displacive Phases and its Effect on the Diffraction Pattern. II. Satellite Reflections

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Abstract

The effect on satellite reflections of the temperature variation of the static structural modulation in incommensurate phases is studied. A structural model is introduced that includes the anharmonicity described by the soliton density and follows the assumptions and predictions of the Landau theory generalized to incommensurate phases. Within these premises, a simulation of the diffraction pattern as a function of temperature of Rb_2ZnCl_4 has been carried out. It is shown that the intensity of satellites does not always decrease monotonically with their order and its temperature dependence varies, depending on the satellite, so that it cannot be reduced to a common effective power law. Satellites of first order, for instance, can decrease or increase near the lock-in transition, depending on the particular reflection considered. A simple method for measuring the soliton density is proposed that is based on the expected correlation of the intensities of close first-order and higher-order satellites. Finally, the effect that high-order harmonics can have in a standard refinement of an incommensurate structure near the lock-in transition is discussed.

1. Introduction

In the preceding paper (Aramburu, Madariaga & Pérez-Mato, 1997), hereafter denoted I, an expression for the atomic scattering modulation factors $g^\mu(\mathbf{H})$ in incommensurate (IC) displacive phases in terms of the amplitude (ρ) and phase (θ) of the order parameter was presented. Using this expression, the influence of the temperature variation of the static structural modulation on the intensity of main reflections was analyzed. A similar study for satellite reflections is carried out in this paper.

The relation between the temperature dependence of the modulation and the intensity of satellite reflections has been analyzed in the strict soliton limit (Pérez-Mato & Madariaga, 1986) and in the critical region near the normal(N)–incommensurate transition (Majkrzak, Axe

& Bruce, 1980). The lack of general theoretical studies in the whole temperature range between these limits has led to the use of the results only valid for the critical region in the analysis of the variation of satellite intensities in large temperature ranges (clearly outside the critical region), where its applicability is not justified (Andrews & Mashiyama, 1983). The discrepancies between the experimental results and these oversimplified predictions have been sometimes interpreted as a consequence of the effect of overall phason temperature factors (Ehses, 1985). The aim of the present work is to carry out a rigorous study of the effect that the structural modulation changes produce on satellites in the whole stability range of the IC phase.

In the first section, some general rules are obtained concerning the relation between the primary distortion, described by the amplitude and inhomogeneous phase of the order parameter, and the diffraction diagram. In particular, it is shown that satellites of some specific order are specially sensitive to the thermal evolution of the order-parameter configuration and the changes in the soliton density. An approximate expression relating the latter and the relative intensities of pairs of satellites is derived and shown to be a direct and efficient method for the determination of the soliton density. As an illustrative example, the temperature dependence of the diffraction pattern of Rb_2ZnCl_4 is simulated in §3, confirming the general conclusions of the previous section.

Finally, the effect that high-order harmonics can have in a standard refinement of an IC structure near the lock-in transition is discussed. It has usually been assumed that the satellites of a certain order are practically only influenced by harmonics of equal or lower order. According to this assumption, a standard refinement uses as many harmonics in the displacement as the maximum order of satellites detected. In this paper, it will be shown how, sometimes, the structural determination could be improved if additional harmonics of certain orders (not corresponding with the order of satellites detected) are introduced in the refinement.

2. Effect of the temperature dependence of the static modulation on satellite reflections

In the case of an IC phase with a one-dimensional displacive modulation, if only the primary distortion associated with the order parameter is considered, the atomic modulation functions describing the static atomic displacements can be written as follows (Aramburu, Madariaga & Pérez-Mato, 1995):

$$u_\alpha^\mu(v) = \rho u_{1\alpha}^\mu \cos[2\pi\theta(v) + \Psi_{1\alpha}^\mu + \mathbf{q}_L \cdot \mathbf{r}_{av}^\mu],$$
$$\mu = 1, \ldots s, \quad \alpha = \{x, y, z\}, \tag{1}$$

where $\mathbf{r}_{av}^\mu$ is the average position of the atom μ in the unit cell, $\mathbf{q}_L$ is the lock-in wave vector, $\{u_{1\alpha}^\mu, \Psi_{1\alpha}^\mu\}$ are the amplitudes and phases of the first harmonic at a given temperature T_0, v is the internal coordinate and $\{\rho, \theta(v)\}$ represent the amplitude and the inhomogeneous phase of the order parameter, respectively. Using some general properties satisfied by the function $\theta(v)$ [$\theta(-v) = -\theta(v)$ and $\theta(v + 1/r) = \theta(v) + 1/r$, r being the number of domains present in the lock-in phase], the structure factor can be expressed as (see I)

$$F(\mathbf{H}) = \sum_{\mu=1}^{s} f^\mu(H)\mathbf{g}^\mu(\mathbf{H}) \exp(i2\pi\mathbf{H} \cdot \mathbf{r}_{av}^\mu),$$

where

$$g^\mu(\mathbf{H}) = \sum_{m=-\infty}^{\infty} J_{mr-h_4}(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1'^\mu|)$$
$$\times \exp[i(mr - h_4)(\varphi_1^\mu + \pi/2)]I_{h_4}^{mr-h_4}, \tag{2}$$

$$u_{1\alpha}'^\mu \equiv (u_{1\alpha}^\mu/2) \exp[i(\Psi_{0\alpha}^\mu + \mathbf{q}_L \cdot \mathbf{r}_{av}^\mu)]$$

and

$$I_{h_4}^{mr-h_4} \equiv \int_0^1 \cos\{2\pi[(mr - h_4)\theta(v) + h_4 v]\} \, dv.$$

$\mathbf{H} = \mathbf{G} + h_4\mathbf{q}_I$, where $\mathbf{G}$ is any reciprocal vector of the normal phase structure, h_4 any integer and $\mathbf{q}_I$ the wave vector of the one-dimensional IC modulation. $|\mathbf{H} \cdot \mathbf{u}_1'^\mu|$ and φ_1^μ represent the amplitude and phase of the complex dot product $\mathbf{H} \cdot \mathbf{u}_1'^\mu$, respectively. According to the parameterization of the primary distortion (1), the $g^\mu(\mathbf{H})$ are functions of the amplitude ρ and the inhomogeneous phase $\theta(v)$ of the order parameter. The anharmonicity in the modulation is determined by the shape of the function $\theta(v)$. This shape is controlled by the soliton density n_s (Bruce, Cowley & Murray, 1978) through the sine–Gordon differential equation (Bak & Emery, 1976; Tolèdano & Tolèdano, 1987; Aramburu, Madariaga & Pérez-Mato, 1995).

Near the N–IC transition temperature (T_I), only the first harmonic is present in the structural modulation (sinusoidal limit). Since $n_s = 1$, $\theta(v) = v$ and $I_{h_4}^{mr-h_4} = \delta_{m,0}$. In consequence, the expression for $g^\mu(\mathbf{H})$ becomes particularly simple:

$$g^\mu(\mathbf{H}) = \exp[-ih_4(\varphi_1^\mu + \pi/2)]J_{-h_4}(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1'^\mu|).$$

On the other hand, in the so-called soliton limit, $\theta(v)$ is a step function $[\theta(v) = (2j - 1)/2r; \ (j - 1)/r \le v \le j/r$ $(j = 1, \ldots, r)]$ and a simple analytical expression for $g^\mu(\mathbf{H})$ can be also obtained.
If $h_4 = nr$ $(n \ne 0)$:

$$I_{nr}^{(m-n)r} = 0 \ \forall m \Rightarrow g^\mu(\mathbf{H}) = 0 \ \forall\mathbf{G};$$

if $h_4 \ne nr$:

$$I_{h_4}^{mr-h_4} = (-1)^m[\sin(\pi h_4/r)/(\pi h_4/r)] \ \forall m;$$

and, therefore,

$$g^\mu(\mathbf{H}) = \exp(-i\pi h_4/r)[\sin(\pi h_4/r)/(\pi h_4/r)]$$
$$\times \left\{ (1/r) \sum_{j=1}^{r} \exp[i2\pi(\mathbf{H} \cdot \mathbf{u}_j^\mu + jh_4/r)] \right\},$$

where $\mathbf{u}_j^\mu$ are the values of the displacement in the jth domain $[\theta(v) = (2j - 1)/2r$ in (1)]. These expressions coincide with those deduced by Pérez-Mato & Madariaga (1986) in a more general context for arbitrary $\mathbf{u}_j^\mu$. According to this expression, satellites whose order is a multiple of r will vanish in this limit. A particular case of this general rule can be found in the early analysis by Böhm (1975) of very simplified commensurate modulations. Therefore, it is expected that satellites of these orders can hardly be detected in the whole stability range of the IC phase. This is what happens, for example, in the case of the sixth-order satellites in Rb_2ZnCl_4 $(r = 6)$ (Andrews & Mashiyama, 1983).

Although the expression for $g^\mu(\mathbf{H})$ is rather simple in the sinusoidal and soliton limits, in the intermediate region, the expression becomes more complex, with several terms in the sum (2). Nevertheless, some general conclusions can be derived:

(i) The Bessel function of first order J_1 appears in (2) only for satellites of order $|h_4| \in \{1, mr \pm 1 \ (m \in Z^+)\}$ if $r > 2$ or $|h_4| \in \{1, 2m + 1 \ (m \in Z^+)\}$ if $r = 2$. These exactly correspond with the order of the harmonics involved in the progressive built up of the r domains to appear in the lock-in phase (primary distortion) (Aramburu, Madariaga & Pérez-Mato, 1995). As, for $x \ll 1$, $J_n(x) \simeq x^n$, it is expected that these satellites would show unexpectedly strong intensities in comparison to the rest, including satellites of lower order. This is what happens with third-order satellites in thiourea $(r = 2)$ (Zúñiga et al., 1989) or fifth- and seventh-order satellites in Rb_2ZnCl_4 $(r = 6)$ (Andrews & Mashiyama, 1983; Aramburu, Madariaga, Grebille, Pérez-Mato & Breczewski, 1997).

(ii) According to the order of the Bessel functions appearing in (2) $(n = mr - h_4, m \in Z)$, it is expected that the number of relevant terms in (2) decreases when r increases. That is to say, for a fixed satellite order, the expression for $g^\mu(\mathbf{H})$ will be, in principle, simpler in compounds with high r. Thus, in the case of the first-

order satellites in thiourea ($r = 2$), four Bessel functions of order $n = -1, 1, -3, 3$ contribute in a significant form to $g^\mu(\mathbf{H})$ for $4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1'| \simeq 3$, while, in the case of Rb_2ZnCl_4 ($r = 6$), in the same conditions only one term ($n = -1$) is non-negligible.

(iii) A handy way to quantitatively characterize the temperature dependence of the intensities is by means of the so-called effective exponents (β_{eff}), defined as $I(\mathbf{H}, t) = I_0 t^{\beta_{eff}}$, where $t \equiv T_I - T$. As the atomic displacements increase and new terms become significant in (2), the relation between the effective exponents ($\beta_{eff,n}$) of the nth-order satellites and the effective exponent (β) of the order parameter [$\rho(t) = \rho_0 t^\beta$] becomes quite complex. The expression $\beta_{eff,n} \simeq 2n\beta$ obtained in the limit of small displacements is no longer valid, as observed experimentally in Rb_2ZnCl_4 (Andrews & Mashiyama, 1983; Aramburu, Madariaga, Grebille et al., 1997).

(iv) When n_s decreases, the value of the integral $I_{r-1}^{-(r-1)}(n_s)$ [which is, as seen above, the only non-zero term in the strict sinusoidal regime ($n_s = 1$)] also decreases but, on the other hand, $I_{r-1}^1(n_s)$ increases; high values of r favor this effect. Thus, if r is sufficiently high ($r \geq 6$), it is expected that for satellites of order ($r - 1$) only the term corresponding to J_1 appreciably contributes in (2) for an $n_s \neq 1$. Moreover, if the value of r is high enough, only the first term (corresponding to J_{-1}) will contribute to the $g^\mu(\mathbf{H})$ of the first-order satellites. Consequently, for $r \geq 6$:

(a) The effect of n_s on the structure factor of satellites of order 1 and ($r - 1$) will be limited to the appearance of a global temperature-dependent factor for each satellite order [$I_1^{-1}(r, n_s)$ and $I_{r-1}^1(r, n_s)$, respectively]. For example, in the case of Rb_2ZnCl_4,

$$g^\mu(\mathbf{G}, h_4 = 1) \cong J_{-1}(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1''^\mu|)$$
$$\times \exp[-i(\varphi_1^\mu + \pi/2)]I_1^{-1}(n_s)$$
$$g^\mu(\mathbf{G}', h_4' = 5) \cong J_1(4\pi\rho|\mathbf{H}' \cdot \mathbf{u}_1''^\mu|)$$
$$\times \exp[i(\varphi_1^\mu + \pi/2)]I_5^1(n_s).$$

Note that the factors $I_1^{-1}(n_s)$ and $I_5^1(n_s)$ are common for all atoms.

(b) If each first-order satellite $\mathbf{H} = (\mathbf{G}, h_4 = 1)$ is matched up with an ($r - 1$)th-order satellite $\mathbf{H}' = (\mathbf{G}', h_4' = r - 1)$, so that $\mathbf{G} + \mathbf{q}_L = \mathbf{G}' + (r - 1)\mathbf{q}_L$, then $\mathbf{H} \simeq \mathbf{H}'$ and the quotient between their structure factors will be approximately the same for all pairs. Thus, in the case of Rb_2ZnCl_4,

$$|F(\mathbf{H}')|/|F(\mathbf{H})| \cong [I_5^1(n_s)/I_1^{-1}(n_s)] = f(n_s). \quad (3)$$

As n_s decreases, the function $f(n_s)$ increases, up to a value of ~ 0.2 in the soliton limit ($n_s = 0$), in agreement with the value obtained by Pérez-Mato & Madariaga (1986) ($h_4/h_4' = \frac{1}{5}$). This result is especially interesting because, in principle, it makes possible a direct determination of the function $n_s(T)$ in the temperature

range for which satellites of ($r - 1$)th order have been observed.

All previous results have been derived from the functional form (2) obtained for $g^\mu(\mathbf{H})$ when only harmonics with the symmetry of the order parameter are considered. Although this primary distortion is expected to be the most important in the structural modulation, harmonics of other symmetries compatible with the superspace group of the IC phase will also be present and, in general, will not be negligible compared with the primary distortion. This is the case of the second-harmonic modulation determined in the IC phase of thiourea (Zúñiga et al., 1989) or the third-harmonic modulation in Rb_2ZnCl_4 (Aramburu, Madariaga, Grebille et al., 1997). The presence of this secondary distortion involves an additional complication of the functional form of $g^\mu(\mathbf{H})$. For example, if an nth harmonic corresponding to a secondary distortion is included in the description of the structural modulation,

$$u_\alpha^\mu(\nu) = \rho u_{1\alpha}^\mu \cos[2\pi\theta(\nu) + \Psi_{1\alpha}^\mu + \mathbf{q}_L \cdot \mathbf{r}_{av}^\mu]$$
$$+ \rho' u_{n\alpha}^\mu \cos(2\pi n\nu + \Psi_{n\alpha}^\mu + n\mathbf{q}_L \cdot \mathbf{r}_{av}^\mu). \quad (4)$$

The atomic scattering modulation functions will be expressed as

$$g^\mu(\mathbf{H}) = \sum_{m=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} J_{mr-h_4'}(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1''^\mu|)J_l(4\pi\rho'|\mathbf{H} \cdot \mathbf{u}_n''^\mu|)$$
$$\times \exp\{i[(mr - h_4')(\varphi_1^\mu + \pi/2)$$
$$+ l(\varphi_n^\mu + \pi/2)]\}I_{h_4'}^{mr-h_4'},$$

where $h_4' \equiv h_4 + tn$ ($t \in Z$) and $I_{h_4'}^{mr-h_4'}$ is defined as in (2). Satellites of nth order will, therefore, be strongly influenced by the presence of this new harmonic in the structural modulation and, to a lesser extent, the ($n - 1$)th and ($n + 1$)th satellites. In general, the presence of a non-negligible secondary distortion in the modulation complicates the relation between the structural change and the experimental β_{eff}, as a new polarization vector $\{u_{n\alpha}^\mu, \Psi_{n\alpha}^\mu\}$ together with its corresponding effective exponent (β') will now also be involved. Furthermore, deviations from the general intensity correlations such as that given by (3) in Rb_2ZnCl_4 are expected.

In order to verify all these qualitative results, the temperature dependence of the diffraction diagram of Rb_2ZnCl_4 in its IC phase has been simulated. Owing to the high value of r (6) in this compound, relatively simple expressions for $g^\mu(\mathbf{H})$ are expected, while the detection of high-order satellites (fifth and seventh) (Andrews & Mashiyama, 1983; Aramburu, Madariaga, Grebille et al., 1997) indicates the presence of a strong soliton regime in the structural modulation. The approximated temperature dependence of the structural distortion in this compound, including the soliton density, has been recently determined (Aramburu, Madariaga, Grebille et al., 1997). This simulation

will allow us not only to verify the qualitative results previously discussed but also to carry out quantitative predictions (about the $\beta_{\text{eff},n}$, for example) than can be experimentally tested. The results are shown in the next section.

3. Simulation of the temperature dependence of the diffraction pattern for Rb_2ZnCl_4

The temperature dependence of the structural modulation in Rb_2ZnCl_4 has been characterized by means of three parameters: the global amplitude (ρ) of the primary distortion, the soliton density (n_s) and the amplitude (ρ') of the third harmonic (secondary distortion) [$n = 3$ in (4)]. The temperature variation of these parameters has been determined in a previous paper (Aramburu, Madariaga, Grebille *et al.*, 1997) and is able to reproduce the observed temperature behavior of some selected main reflections and satellites up to seventh order. Using this structural model, the intensities of the stronger satellite reflections of each order with $|\mathbf{H}| \leq 1.6\,\text{Å}^{-1}$ (up to a total of 6991 reflections) have been generated at 13 temperatures between $T_I = 303$ and $T_L \simeq 195\,\text{K}$. The polarization vector of the primary distortion and anisotropic thermal parameters were taken from the experimental IC structure determined by Hedoux, Grebille, Jaud & Godefroy (1989). The third harmonic was that estimated by Aramburu, Madariaga, Grebille *et al.* (1997). The anisotropic displacement parameters were corrected at each temperature following a linear law. For every symmetry-independent atom, the amplitudes of a Fourier expansion of (4) in terms of the variable $t = v + \mathbf{q}_L \cdot \mathbf{r}^\mu$ were introduced in the program *REMOS* (Yamamoto, 1982) in order to generate the intensities. By construction, only harmonics of order $1, 3, 6m \pm 1$ $(m \in Z^+)$ appeared in the expansion. Satellites up to seventh order were calculated. Owing to the weakness obtained for sixth-order satellites (as corresponds to a compound with $r = 6$), they were not considered in subsequent studies.

3.1. Temperature dependence of the effective exponents $(\beta_{\text{eff},n})$

The effective exponents depend on the temperature and the particular reflection ($\mathbf{H}$) considered. For every reflection, the corresponding value of the effective exponent at the temperature T_i $(i = 2, \ldots, 12)$ has been obtained from the variation of the intensity in the range $T_{i-1}, \ldots, T_{i+1}$. For a fixed satellite order $(n,$ for example), the β_{eff} obtained at T_i are distributed in a range of values. This distribution is approximately Gaussian and has been characterized through the mean value $\langle \beta_{\text{eff},n} \rangle (T_i)$ and the mean absolute deviation $(1/N)\sum_{j=1}^{N}|\beta_{\text{eff}}(\mathbf{H}_j)(T_i) - \langle \beta_{\text{eff},n} \rangle (T_i)|$, N being the number of nth-order satellites. In this averaging

process, only reflections whose intensity surpasses a certain value in the whole range $T_{i-1}, \ldots, T_{i+1}$ have
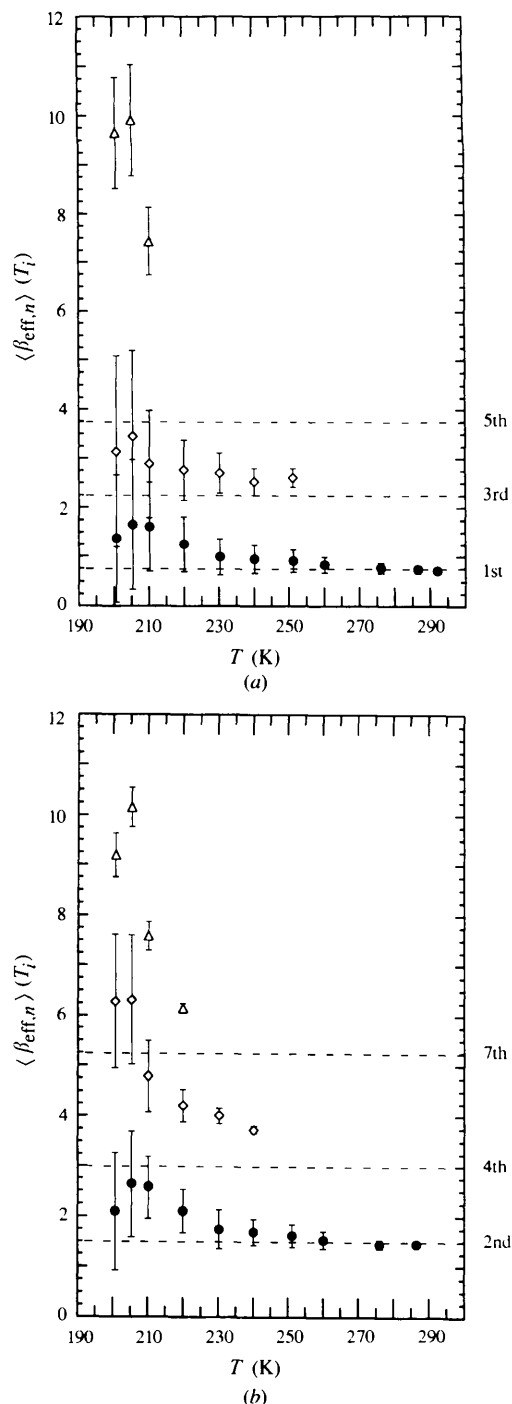

Fig. 1. Temperature dependence of the mean effective exponents $\langle \beta_{\text{eff},n} \rangle$ for (a) first- (circles), third- (rhombs) and fifth- (triangles) order satellites; (b) second- (points), fourth- (rhombs) and seventh- (triangles) order satellites. The error bars indicate the mean absolute deviation of $\beta_{\text{eff},n}(T_i)$ from the mean value $\langle \beta_{\text{eff},n} \rangle (T_i)$ (see text) and the discontinuous lines the values close to T_i [$2n\beta$; $\beta = 0.37$ for $T \geq 220\,K$ (Aramburu, Madariaga, Grebille *et al.*, 1997)].

been considered. As threshold value, we take the intensity determined for the (6015) satellite at 220 K in the experiment reported by Aramburu, Madariaga, Grebille *et al.* (1997). The $\langle \beta_{eff.n} \rangle (T_i)$ thus obtained are shown in Figs. 1(a) and (b). It can be observed that, at the temperature at which high-order satellites are 'sufficiently' strong to be detected, the difference between $\langle \beta_{eff.n} \rangle$ and $2n\beta$ is large (around 20% for third-, fourth- and seventh-order satellites, and even 100% in the case of the fifth-order satellites), increasing further at lower temperatures. For satellites of first and second order, this difference is small near T_I ($\sim 3\%$) but begins to be important 50 K below that temperature (around 20 and 10%, respectively). The bars in Figs. 1(a) and (b) represent the mean absolute deviation from the mean value. It can be observed that, when the temperature is lowered, the variety of behaviors shown by the satellites of nth order increases, this effect being higher for satellites of lowest orders. In fact, $\beta_{eff.1}(T = 200\,\mathrm{K}, \mathbf{H}) = 1.37\,(129)$, so that in this region the character (increasing, decreasing or constant) of the temperature dependence of the intensity will depend on the particular first-order satellite selected (see Fig. 2). This dispersion of values is already obtained when only a first harmonic is introduced in the structural model and no Debye–Waller thermal factor is considered, so this is not only a consequence of the effect of ρ', n_s or the anisotropic thermal factors. As can be seen in Fig. 1, the β calculated from the experimental $\beta_{eff.n}(\mathbf{H})$ of a particular reflection through $\beta \cong \beta_{eff.n}(\mathbf{H})/2n$ can only be significant in the case of the first- and second-order satellites, and this only in a range of about 20 K below T_I.

3.2. Relation between the intensities of the first- and fifth-order satellites and evaluation of the soliton density

At every temperature, the quotient of (3) has been calculated for every pair of reflections $\mathbf{H} =$
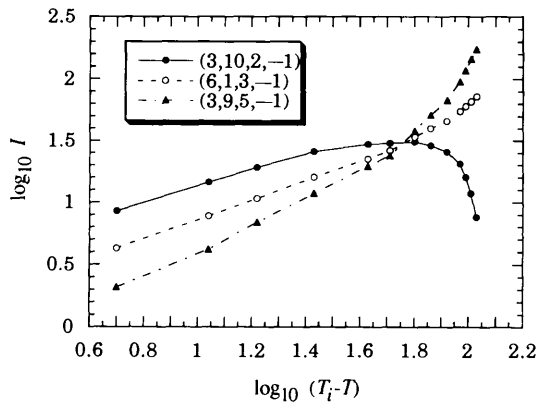
$(\mathbf{G}, h_4 = \pm 1)$ and $\mathbf{H}' = (\mathbf{G}', h_4' = \pm 5)$ such that $\mathbf{G} \pm \mathbf{q}_L = \mathbf{G}' \pm 5\mathbf{q}_L$, where $\mathbf{q}_L$ is the lock-in wavevector $\mathbf{q}_L = \frac{1}{3}\mathbf{c}^*$. The distribution of the values obtained has been characterized by its mean value and the mean absolute deviation. The average value obtained for every temperature is represented with an open symbol in Fig. 3. The theoretical values determined according to the quotient $I_5^1(n_s)/I_1^{-1}(n_s) = f(n_s)$ are also shown (crosses). In the case that only primary distortion (harmonics 1, 5, 7, ...) is considered (open circles), the equality (3) is exactly satisfied. Moreover, at a fixed temperature, the dispersion of values around the average is very reduced. In Fig. 3, only the maximum mean absolute deviation, which is obtained at the lowest temperature, is represented (shorter bar). When
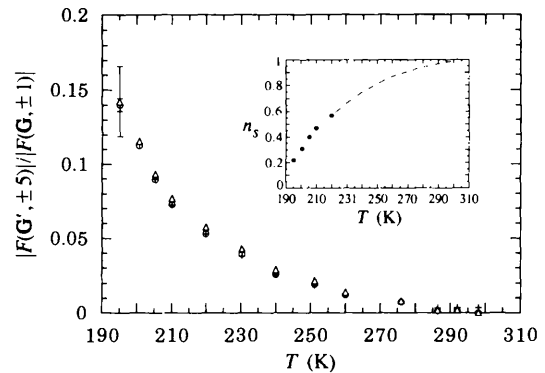

Fig. 3. Average relation between the moduli of the structure factors of the first- and fifth-order satellites in Rb_2ZnCl_4. Each pair of reflections has been selected so that $\mathbf{G} \pm \mathbf{q}_L = \mathbf{G}' \pm 5\mathbf{q}_L$. Only the 212 strongest fifth-order satellites have been considered in the calculation. The approximate values predicted by (3) are represented with crosses, while the results obtained from the *REMOS* calculation are indicated with open circles (only primary distortion) or triangles (secondary distortion included). The maximum mean absolute deviation is obtained at the lowest temperature, being the only one represented (error bar). The inset shows the function $n_s(T)$ used in the simulation (Aramburu, Madariaga, Grebille *et al.*, 1997).
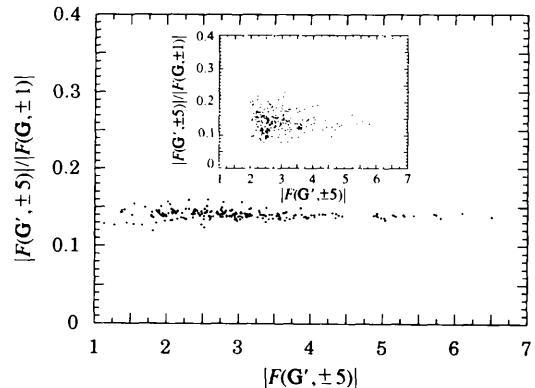

Fig. 2. log–log plot of the simulated temperature variation of the intensity for some first-order satellites of Rb_2ZnCl_4. A large variety of behaviors near T_L is clearly observed.

Fig. 4. Set of ratios between the structure factors of the first- and fifth-order satellites at $T = 195$ K. The strong correlation existing when only the primary distortion is considered (main picture) disappears when the secondary distortion is introduced (inset).

the third harmonic (secondary distortion) is introduced in the structural model, the mean value of the quotient is also very near the theoretical value at every temperature (triangles) but the mean absolute deviation increases a lot (large bar at the lowest temperature). As $f(n_s)$ is very sensitive to the value of n_s, the great dispersion of values obtained in this case will imply a high error in the evaluation of n_s if this is done from a single intensity ratio. This loss of correlation between the intensities of the first- and fifth-order satellites caused by a secondary structural distortion can be clearly observed in Fig. 4. It can therefore be concluded that, if only the primary distortion is significant in the structural modulation, (3) provides a direct and precise way to determine the temperature dependence of n_s, even when only a reduced number of fifth-order satellites is measured. On the contrary, if a secondary distortion appreciably contributes to the structural modulation, (3) has only a statistical validity and can be used for the determination of n_s using average values of the ratio for a considerable number of satellite pairs.

3.3. Influence of high-order harmonics on the intensity of satellite reflections

The weight of the harmonics in the structural modulation does not necessarily decrease monotonically with the harmonic order. Thus, in Rb_2ZnCl_4, for example, the second and fourth harmonics are practically negligible compared with the third or the fifth ones (Aramburu, Madariaga, Grebille et al., 1997). In that case, satellites of a certain order (n, for example) can be strongly influenced by harmonics in the modulation of order $m > n$. In order to study the average effect on nth-order satellite reflections of mth-order harmonics with $m > n$ in Rb_2ZnCl_4, we proceeded as follows:

(i) As 'observed' structure factors, those generated with the complete structural model were used: ρ' (harmonic 3); ρ and n_s (harmonics 1, 5, 7).

(ii) As 'calculated' structure factors, we considered either those generated using only the first harmonic in the modulation or those obtained using the first and third harmonics. For each satellite order, i, a conventional agreement factor $R_i = \sum_{n_i} ||F_{o,n_i}| - |F_{c,n_i}|| / \sum_{n_i} |F_{o,n_i}|$ has been calculated using the program $REMOS$ (Yamamoto, 1982). A comparison between 'calculated' and 'observed' structure factors will furnish, in the first case, information about the combined effect of the harmonics 3, 5 and 7 on the first- and second-order satellites (see Fig. 5a) and, in the second case, the influence of n_s (harmonics 5, 7) on satellites of order less than or equal to 4 (see Fig. 5b).

A comparative analysis between Figs. 5(a) and (b) shows the strong influence of the third harmonic on second- and even first-order satellites. The effect of n_s is, instead, particularly high for third- and fourth-order satellites. These effects cannot be balanced out by means of a partial scale factor. Only in the case of the fourth-order satellites does the refinement of the scale factor give rise to a significant decrease in the value of R (see half-bars in Fig. 5a,b).

According to the previous results, it can be concluded that the influence of the mth-order harmonics on the nth-order satellites with $n < m$ can sometimes be high, especially near the lock-in transition. Therefore, if after the standard refinement of an IC structure near T_L, using as many harmonics as order of satellites detected, the final R_i factors remain high, one of the causes may be a significant presence of higher-order harmonics in the modulation, even if satellites of this order are too weak to be measured. A more accurate description of the global distortion could be obtained if those higher harmonics were included in the refinement. Let us suppose, for example, that in a measurement carried out in Rb_2ZnCl_4 at 195 K only first-order satellites had been measured. If, according to the standard procedure, only a first harmonic were included in the structural modulation, one should expect a residual disagreement in the first-order satellites of around 10% (see Fig. 5a).
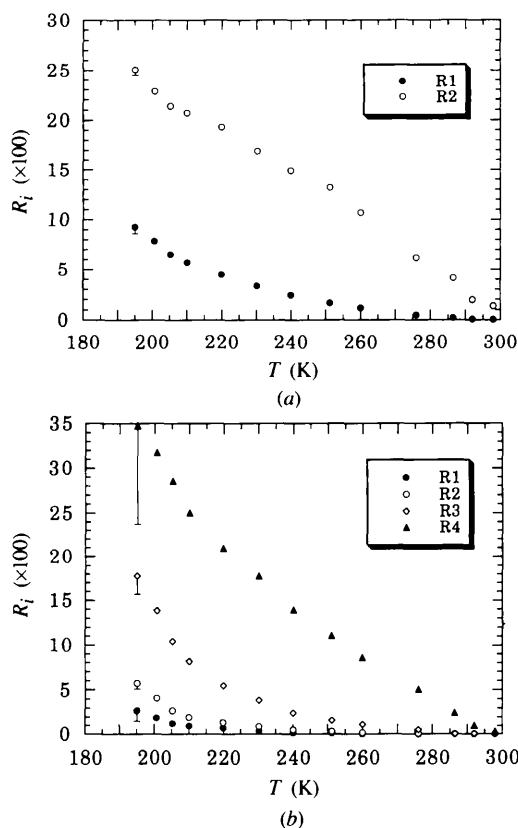

Fig. 5. Temperature dependence of the partial agreement R_i factors when (a) only the first harmonic has been used to generate the 'calculated' structure factors; (b) the third harmonic has also been considered (see text). When a partial scale factor is refined for each satellite order, the maximum decrease in the value of R_i is obtained at the lowest temperature, being the only one represented (half-bar).

Besides, the insertion of a second harmonic would not significantly improve the refinement as the distortion corresponding to this harmonic is negligible even in the lock-in phase (Aramburu, Madariaga, Grebille et al., 1997). Only when a third harmonic is considered in the structural refinement can the disagreement be reduced to 3% (see Fig. 5b).

4. Conclusions

The effect on satellite reflections of the temperature dependence of the static modulation in displacive IC phases has been studied. It has been shown that, if the modulation can be approximately reduced to the one originated by the order parameter, the satellites of order $\{mr \pm 1 \ (m \in Z^+)\}$ in compounds with $r > 2$ [$\{2m + 1$ $(m \in Z^+)\}$ in compounds with $r = 2$] will show a high intensity in comparison to that of lower-order satellites. On the contrary, satellites whose order is a multiple of r will be very weak. The relation between the temperature variation of the intensities (characterized by means of the effective exponents β_{eff}) and the structural change [characterized by the effective exponent β and the function $n_s(T)$] is not simple. In fact, a simulation of the temperature dependence of the IC diffraction pattern of Rb_2ZnCl_4 shows that the values of $\beta_{eff,n}$ that can be determined in an experimental measurement appreciably differ from those obtained close to the IC transition temperature $(2n\beta)$. Moreover, except in the case of first- and second-order satellites very near T_I, the temperature variation of the intensity is not similar for all satellites of a fixed order: there is a great dispersion of values, even if only the first harmonic is considered in the modulation. Therefore, the determination of the structural change [$\beta(T), n_s(T)$] from the experimental β_{eff} of some reflections is in general not feasible. It will be necessary to have additional information about the harmonics that participate in the structural distortion, their polarization vectors and the anisotropic thermal parameters.

On the other hand, it has been shown how, in compounds with a high value of r ($r \geq 6$), a correlation between the intensities of the first- and the $(r - 1)$th-order satellites exists. In particular, for a given temperature, the value of the quotient between the intensities of every pair of reflections that superimpose at T_L is the same for all of them: it only depends on n_s. This approximate relation can be used as a simple and efficient method to determine the soliton density and it is even valid when secondary distortions are significant, if used as an average expression.

Finally, it has been shown that the effect of the harmonics not considered in a standard refinement because satellites of such high order are too weak to be systematically detected can sometimes be important. This effect cannot be balanced with partial scale factors. Therefore, large values for the R_i factors obtained in a standard refinement near the lock-in transition could indicate a non-negligible contribution of higher-order harmonics to the modulation. If these harmonics were introduced in a new refinement of the structure, lower values for the R_i factors and an improvement in the structural determination can be, in principle, obtained.

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