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

I. Aramburu,[a]* G. Madariaga[b] and J. M. Pérez-Mato[b]

[a]*Departamento Física Aplicada I, Escuela Técnica Superior de Ingenieros Industriales y de Telecomunicación, Universidad del País Vasco, Alameda de Urquijo s/n, 48013 Bilbao, Spain, and* [b]*Departamento Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain. E-mail: wmbarlei@lg.ehu.es*

Abstract

The effect of the temperature dependence of the structural modulation on the intensity of main reflections is analyzed. A simple expression for the atomic scattering modulation factors has been derived describing the structural distortion in terms of the amplitude and the inhomogeneous phase of the order parameter. According to this expression, some main reflections can be strongly influenced by modulation harmonics. Owing to this influence, the intensity of some main reflections can increase, decrease or even show a pronounced minimum as the temperature is lowered. These results are experimentally verified in thiourea.

1. Introduction

The diffraction pattern of an incommensurate (IC) phase is characterized by the appearance of satellites near the main reflections corresponding to a high-temperature normal phase (N). The intensity of these satellite reflections does not usually remain constant in the whole stability range of the IC phase. As the temperature approaches the lock-in transition temperature (T_L) at which the wave vector is locked into a rational value, the intensity of satellites usually increases. In the case of IC phases with a displacive modulation, this is fundamentally due to the temperature variation of the static structural distortion. Near the N–IC transition temperature (T_I), the structural modulation can be described by a harmonic displacement field of wave vector $q_I(T)$ (sinusoidal limit). However, when the temperature is lowered, it is expected that the amplitude of the first harmonic increases and new harmonics of higher order progressively arise in the structural modulation, in order to produce the continuous appearance of the lock-in domains (soliton limit). The effect of the structural modulation on the intensity distribution of satellite reflections has been analyzed only in both limits, where the atomic displacement field is easy to describe (Pérez-Mato & Madariaga, 1986). The utility of these results is, however, very reduced:

the soliton limit has never been experimentally detected, while the result obtained for the sinusoidal limit will fail when new harmonics appreciably contribute to the structural modulation. With regard to the main reflections, it has usually been assumed that the temperature dependence of the structural modulation does not strongly affect their intensities, and their possible variation is mainly due to changes in the average structure. The aim of the present work is to analyze the effect that the changes in the static modulation produces on main reflections and satellites in the whole stability range of the IC phase. The application of a model that describes the structural change together with the analysis of the effect on main reflections is carried out in this paper, while the study of the satellite reflections is presented in a subsequent paper (Aramburu, Madariaga & Pérez-Mato, 1997).

In the first section, the structural distortion is parameterized in terms of the amplitude and the inhomogeneous phase of the order parameter. For simplicity, only one-dimensional modulations have been considered. With this structural model, a simplified expression for the atomic scattering modulation factors has been obtained. An analysis of this expression (supported by the simulation of the intensity of several main reflections in two specific compounds) reveals that, unlike what has been usually assumed, some main reflections not only are strongly influenced by changes in the structural modulation but they show surprising behavior when the temperature is decreased. A measurement of the temperature dependence of the intensity of some main reflections in thiourea confirms these results.

2. Structural model and atomic scattering modulation factors

The structure factor of an IC displacive structure with a one-dimensional modulation can be expressed (neglecting the thermal factor) as

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

where

$$g^{\mu}(\mathbf{H}) = \int_{0}^{1} d\nu \exp\{i2\pi[\mathbf{H} \cdot \mathbf{u}^{\mu}(\nu) + h_4\nu]\} \qquad (2)$$

are the so-called atomic scattering modulation factors (Pérez-Mato, Madariaga & Tello, 1986; Pérez-Mato, Madariaga, Zúñiga & García Arribas, 1987) that modify the atomic scattering factors $f^{\mu}(H)$ of the s atoms located at the average positions $\mathbf{r}_{av}^{\mu}$ in the unit cell of the N phase. $\mathbf{H} = \mathbf{G} + h_4\mathbf{q}_I$, where $\mathbf{G}$ is any reciprocal vector of the basic structure, h_4 any integer and $\mathbf{q}_I$ the wave vector of the IC modulation. The effect of the atomic displacements is, therefore, included in the factor $g^{\mu}(\mathbf{H})$ through the atomic modulation functions $\mathbf{u}^{\mu}(\nu)$ periodic along the internal coordinate ν (Pérez-Mato *et al.*, 1987). Each value of ν in the range [0,1] represents a certain cell (**l**) in direct space according to: $\mathbf{u}(\mu, \mathbf{l}) = \mathbf{u}^{\mu}(\nu = \mathbf{q}_I \cdot \mathbf{l})$.

Within the so-called constant-amplitude approximation (Shiba & Ishibashi, 1978; Blinc, Prelovsek & Kind, 1983), the structural modulation can be expressed (Aramburu, Madariaga & Pérez-Mato, 1995) as

$$u_{\alpha}^{\mu}(\nu) = \rho u_{1\alpha}^{\mu} \cos[2\pi\theta(\nu) + \Psi_{1\alpha}^{\mu} + \mathbf{q}_L \cdot \mathbf{r}_{av}^{\mu}],$$
$$\alpha = \{x, y, z\}, \quad \mu = 1, \dots, s, \qquad (3)$$

where $\mathbf{q}_L$ is the lock-in wave vector and $\{u_{1\alpha}^{\mu}, \Psi_{1\alpha}^{\mu}\}$ are the amplitudes and phases of the first harmonic at a given temperature T_0. ρ and $\theta(\nu)$ represent the amplitude and the inhomogeneous phase of the order parameter when the lock-in phase has been taken as reference and are independent of α and μ. ρ is related to the amplitude of the first harmonic and, by construction, is equal to 1 at T_0, increasing at lower temperatures. The shape of $\theta(\nu)$ determines the degree of anharmonicity in the modulation. Near T_I, $\theta(\nu) = \nu$ and the distortion (3) is harmonic. As the temperature is lowered, it aquires a progressive stepped shape to constitute in the soliton limit the r perfect steps that determine the domains of the lock-in phase. It can be demonstrated (Aramburu, Madariaga & Pérez-Mato, 1995) that, in general, the function $\theta(\nu)$ satisfies to a good approximation the sine-Gordon equation:

$$(d\theta/d\nu)^2 = (1/n_s^2)[1 - k^2 \cos^2(2\pi r\theta/2)], \qquad (4)$$

where n_s is the so-called soliton density (Bruce, Cowley & Murray, 1978), which is related to k through $n_s = \pi/2K(k)$, $K(k)$ being the complete elliptic integral of the first kind. Therefore, once the phason degree of freedom is fixed [hereafter we will assume $\theta(0) \equiv 0$], $\theta(\nu)$ will be completely characterized through the soliton density n_s. In the sinusoidal limit, $n_s = 1$ and, in the soliton limit, $n_s = 0$. It must be pointed out that in (3) the structural distortion has been reduced to harmonics

with the same eigenvector as the first one (the order parameter) and, therefore, with the same symmetry. This corresponds to a Landau model where the presence of secondary modes with different symmetries has been neglected. For compounds with $r > 2$, this primary distortion will involve harmonics of orders $\{1, mr \pm 1; m \in Z^+\}$ ($\{1, 2m + 1; m \in Z^+\}$ for compounds with $r = 2$) (Aramburu, Madariaga & Pérez-Mato, 1995). Equations (3) and (4) allow, therefore, the variation of this primary distortion to be simulated by means of the changes in only two parameters, ρ and n_s.

Introduction of (3) in (2) and use of some properties satisfied by the function $\theta(\nu)$ (Aramburu, Madariaga & Pérez-Mato, 1995) mean that the atomic scattering modulation factors can be expressed as

$$g^{\mu}(\mathbf{H}) = \sum_{m=-\infty}^{\infty} J_{mr-h_4}(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1'^{\mu}|)$$
$$\times \exp[i(mr - h_4)(\varphi_1^{\mu} + \pi/2)]I_{h_4}^{mr-h_4}, \qquad (5)$$

where

$$u_{1\alpha}'^{\mu} \equiv (u_{1\alpha}^{\mu}/2) \exp[i(\Psi_{0\alpha}^{\mu} + \mathbf{q}_L \cdot \mathbf{r}_{av}^{\mu})] \qquad (6)$$

and

$$I_{h_4}^{mr-h_4} \equiv \int_{0}^{1} \cos\{2\pi[(mr - h_4)\theta(n_s, \nu) + h_4\nu]\} \, d\nu. \qquad (7)$$

$|\mathbf{H} \cdot \mathbf{u}_1'^{\mu}|$ and φ_1^{μ} represent the amplitude and phase of the complex dot product $\mathbf{H} \cdot \mathbf{u}_1'^{\mu}$, respectively. In (5), the amplitude of the order parameter only appears in the argument of the Bessel functions (the same for all terms in the sum), while the effect of the phase $\theta(\nu, n_s)$ (that is to say, of the degree of anharmonicity in the modulation) is reduced to the functions $I_{h_4}^{mr-h_4}$, independent of the atom μ considered. This expression is, in principle, simpler (it is a particular case) than the general expression given by Pérez-Mato, Madariaga & Tello (1986). This simplicity allows some general consequences to be directly extracted on the effect of the structural variation with temperature on the diffraction pattern. In the next section, it is shown that the influence of the structural change on the main reflections can be sometimes very strong, provoking a pronounced temperature variation in the intensity of some reflections. This result is experimentally confirmed with thiourea. The analysis of the effect on satellite reflections is presented in a subsequent paper.

3. Effect of the temperature dependence of the static modulation on main reflections

For main reflections, Expression (5) of the atomic scattering modulation factors is reduced to

$$g^{\mu}(\mathbf{H}) = J_0(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1^{\prime\mu}|) + \sum_{\substack{m=-\infty \\ m\neq 0}}^{\infty} J_{mr}(4\pi\rho|\mathbf{H} \cdot \mathbf{u}_1^{\prime\mu}|)$$

$$\times \exp[imr(\varphi_1^{\mu} + \pi/2)]I_0^{mr}. \qquad (8)$$

As the indices of the Bessel functions are multiples of r and $J_n(x) \simeq x^n$ for $x \ll 1$, the number of terms that appreciably contribute to (8) should be smaller in compounds with high r. Thus, in the case of Rb_2ZnCl_4 [$r = 6$ (Blinc, Rutar, Topic, Milia & Rashing, 1986; Hedoux, Grebille, Jaud & Godefroy, 1989)], it can be verified that (8) is in practice restricted only to the first term. On the contrary, in the case of thiourea [$r = 2$ (Zúñiga et al., 1989; Aramburu, Madariaga & Pérez-Mato, 1994)], the effect of the second term ($J_2I_0^2$) is also important near the lock-in transition (see, for example, the insets in Figs. 3 and 4). As this term only appears with anharmonic distortions [$I_0^{mr} = 0$ ($m \neq 0$) for $\theta(v) = v$], its significance indicates a non-negligible contribution of high-order harmonics to the intensity of main reflections. In general, in compounds with $r > 2$, the intensity of main reflections is expected to be influenced only by the first harmonic of the primary distortion, while in compounds with $r \leq 2$ the effect of higher-order harmonics (second and/or third) cannot be neglected.

In order to elucidate the sensitivity of the main reflections to the structural change, the intensity of some reflections in the whole stability range of the IC phase of Rb_2ZnCl_4 and thiourea was simulated. As polarization vectors for the primary distortion $\{u_{1\alpha}^{\mu}, \Psi_{1\alpha}^{\mu}\}$, those experimentally determined by Hedoux et al. (1989) and Zúñiga et al. (1989) were, respectively, considered. In the case of Rb_2ZnCl_4, the functions $\{\rho(T), n_s(T)\}$ deduced from experimental data (Aramburu, Madariaga, Grebille, Pérez-Mato & Breczewski, 1997) were used. In the case of thiourea, as the temperature dependence of these parameters has not been yet determined, the relation $\rho(n_s)$ obtained from the minimization process of the free energy (Golovko, 1980; Aramburu, Madariaga & Pérez-Mato, 1994) has been assumed. In consequence, the intensities will be expressed in this latter case as functions of n_s.

An analysis of this simulation reveals that:

(i) The intensity of some main reflections can be strongly influenced by structural changes with various effects. Thus, when the structural modulation evolves towards a more solitonic configuration, their intensities can increase, decrease or remain constant depending on the values of the indices (see Figs. 1 and 2).

(ii) For some reflections, the intensity can even show a pronounced minimum at a certain temperature T' (full dots in the insets of Figs. 3 and 4). The presence of this minimum in the intensity of certain main reflections, i.e. the increase of the intensity for soliton densities lower than $n_s(T')$, seems to be an effect of the harmonics of order greater than 1 [the term $J_2I_0^2$ in

(8)], as can be observed in the insets of Figs. 3 and 4. Thus, in the case of Rb_2ZnCl_4, where only the term J_0 of the expansion (8) appreciably contributes to $g^{\mu}(\mathbf{H})$, deep minima will not be obtained.

The variety of behaviors obtained in the simulation has already been observed in experiments (Aramburu, Madariaga, Pérez-Mato & Breczewski, 1996) and can be used as a test to detect possible structural changes. In fact, it has been useful in the interpretation of the time variation observed in the diffraction pattern of thiourea at 170 K as an evolution of the structural modulation towards a more sinusoidal regime (Aramburu, Madariaga, Pérez-Mato & Breczewski, 1996).

The predicted existence of a minimum in the intensity of the 8400 and 6500 reflections of thiourea (setting $Pnma$) (see insets in Figs. 3 and 4) was checked in a subsequent experiment. The crystal used in the
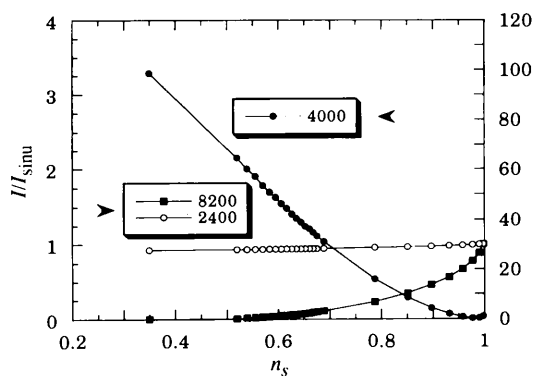

Fig. 1. Evolution with n_s of the intensity of some selected main reflections in thiourea showing different kinds of behaviors when the structural distortion is varied. The intensities have been calculated as given by Aramburu, Madariaga, Pérez-Mato & Breczewski (1996). The intensities have been normalized by the value corresponding to $n_s \simeq 0.997$. The most solitonic regime detected in this compound corresponds to $n_s \simeq 0.67$.
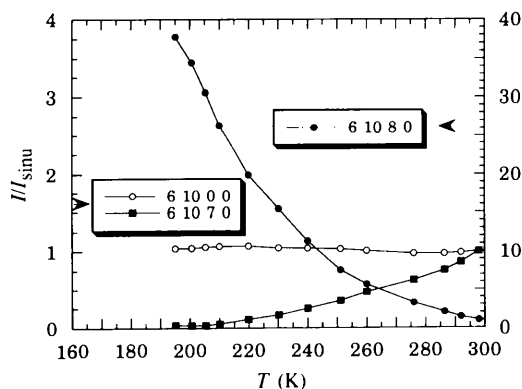

Fig. 2. Temperature dependence of the intensity for some selected main reflections in Rb_2ZnCl_4. The intensities have been calculated from the variation of the structural modulation determined by Aramburu, Madariaga, Grebille, Pérez-Mato & Breczewski (1997). The intensities have been normalized by the value corresponding to $T = 298$ K.

measurements was grown by slow evaporation of an aqueous solution of the purified compound. The X-ray measurements were performed with a CAD-4 diffractometer equipped with an open N_2-gas-flow cryostat (Cosier & Glazer, 1986). The temperature stability was within ±0.2 K. The intensities were measured in $(\omega-\theta)$ scans during a cooling of the sample from T_I to T_L (dots in Figs. 3 and 4). In order to verify the independence of the result obtained and the thermal history of the process, two new measurements were performed: one during a heating from T_L to T_I (squares) and another at 17CX after a direct cooling from the N phase (triangles). Between consecutive measurements, the sample was maintained for about 10 h at 210 K (N phase). The result is independent of the process carried out and, therefore, the variation of the intensity is only a consequence of the structural change. It can be observed in Figs. 3 and 4 that the minimum of the intensity for the 8400 and 6500 reflections of thiourea takes place at different temperatures. Furthermore, the relative positions of the minima are in agreement with the results obtained from the simulation (insets): the minimum of 6500 occurs at a lower temperature, as corresponds to a more solitonic regime. Therefore, a comparison between the functions $I(n_s)$ calculated in the simulation and the curves $I(T)$ experimentally obtained will allow the approximated value of the soliton density to be determined at those temperatures $(T'_1, T'_2, \ldots)$ where the minima are reached [$n_s(T \approx 177\,K) \approx 0.78$; $n_s(T \approx 172\,K) \approx 0.73$].

4. Conclusions

The model of the primary distortion developed by Aramburu, Madriaga & Pérez-Mato (1995) has been used to describe, from the viewpoint of diffraction, the soliton regime characterized by a soliton density n_s, $0 \leq n_s \leq 1$. When the atomic displacement field corresponding to this structural model is introduced in the atomic scattering modulation factors, a rather simple expression is obtained. According to this expression, some main reflections can be strongly influenced by the changes in the structural modulation, especially in compounds with a relatively low number of domains in the lock-in phase ($r \leq 2$). The validity of this assertion has been experimentally verified in thiourea ($r = 2$). In this compound, as the structural modulation tends towards a more solitonic configuration, the intensity of the main reflections can increase, decrease or remain constant, depending on the value of the indices. Moreover, some main reflections (8400 and 6500) can even show a pronounced minimum at a certain temperature. The measurements performed for these reflections clearly indicate a structural origin for this behavior: the temperatures at which the minima are reached are reproducible. Besides, the relative locations of the minima are in agreement with those theoretically deduced from the temperature dependence of the structural modulation. An analysis of the influence of the different harmonics indicates that these minima are fundamentally due to the presence of higher-order harmonics in the modulation (the third one in this case). Therefore, main reflections can be not only influenced by changes in the first harmonic but even by higher-order harmonics.

This sensitivity of certain main reflections to changes in the structural modulation can be used in different ways. For example, if main reflections of different behaviors are considered as check reflections in a standard measurement, information about the possible changes with time in the structural modulation may be obtained. The effect of this structural
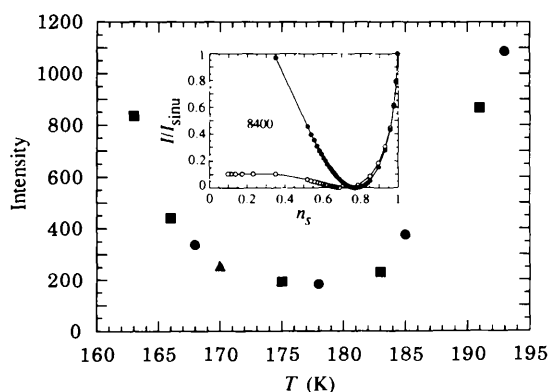

Fig. 3. Intensity of the 8400 reflection in the whole stability range of the IC phase of thiourea (setting *Pnma*). Each symbol type represents measurements performed during the same day: circles, first day (on cooling); triangle, second day (on cooling); and squares, third day (on heating). Between consecutive days, the crystal was maintained for about 10 h at 210 K (normal phase). The inset shows the intensity obtained from the structural model when only the first harmonic of the modulation is considered (empty dots) or all harmonics are taken into account (full dots).
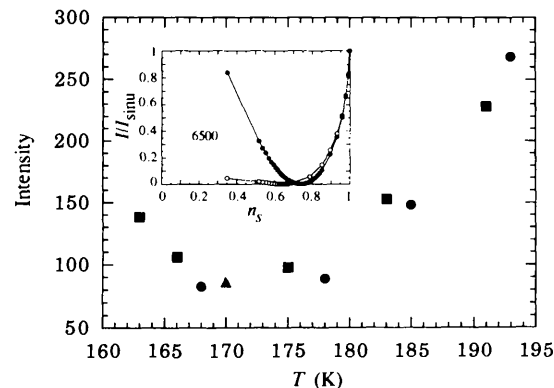

Fig. 4. Intensity of the 6500 reflection of thiourea as a function of temperature (setting *Pnma*). The measurements were carried out as in Fig. 3. The inset contains similar information to that in Fig. 3, showing how this pronounced minimum is related to the presence of harmonics of order greater than 1 in the structural modulation.

change is, at least in thiourea, sufficiently large to prevail on the effects of possible crystal degradation, and it has allowed the determination of the change with time in the structural modulation of this compound (Aramburu, Madariaga, Pérez-Mato & Breczewski, 1996). The presence of a minimum in the intensity of certain main reflections can be used for an approximate determination of the soliton density at the temperatures for which the minima are reached, once an appropriate relation $\rho(n_s)$ (for example, the one supplied by the minimization of the free energy) is assumed.

References

Aramburu, I., Madariaga, G., Grebille, D., Pérez-Mato, J. M. & Breczewski, T. (1997). *J. Phys. I (Paris)*, **7**, 371–383.

Aramburu, I., Madariaga, G. & Pérez-Mato, J. M. (1994). *Phys. Rev. B*, **49**, 802–814.

Aramburu, I., Madariaga, G. & Pérez-Mato, J. M. (1995). *J. Phys. Condens. Matter*, **7**, 6187–6196.

Aramburu, I., Madariaga, G. & Pérez-Mato, J. M. (1997). *Acta Cryst*, A**53**, 334–340.

Aramburu, I., Madariaga, G., Pérez-Mato, J. M. & Breczewski, T. (1996). *Acta Cryst*. A**52**, 203–211.

Blinc, R., Prelovsek, P. & Kind, R. (1983). *Phys. Rev. B*, **27**, 5404–5411.

Blinc, R., Rutar, V., Topic, B., Milia, F. & Rashing, T. (1986). *Phys. Rev. B*, **33**, 1721–1726.

Bruce, A. D., Cowley, R. A. & Murray, A. F. (1978). *J. Phys. C*, **11**, 3591–3608.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Golovko, V. A. (1980). *Sov. Phys. Solid State*, **22**, 1729–1734.

Hedoux, A., Grebille, D., Jaud, J. & Godefroy, G. (1989). *Acta Cryst*. B**45**, 370–378.

Pérez-Mato, J. M. & Madariaga, G. (1986). *Solid State Commun.* **58**, 105–109.

Pérez-Mato, J. M., Madariaga, G. & Tello, M. J. (1986). *J. Phys. C*, **19**, 2613–2622.

Pérez-Mato, J. M., Madariaga, G., Zúñiga, F. J. & García Arribas, A. (1987). *Acta Cryst*. A**43**, 216–226.

Shiba, H. & Ishibashi, Y. (1978). *J. Phys. Soc. Jpn*, **44**, 1592–1599.

Zúñiga, F. J., Madariaga, G., Paciorek, W. A., Pérez-Mato, J. M., Ezpeleta, J. M. & Etxebarria, I. (1989). *Acta Cryst*. B**45**, 566–576.