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Defected structural modulation in the charge density wave compounds 1T-TaS₂ and 1T-TaSe₂

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Résumé. — Nous avons étudié, par microscopie électronique, la formation de défauts de la modulation structurale associée aux ondes de densité de charge (ODC) dans 1T-TaS₂ et 1T-TaSe₂. L'irradiation aux électrons crée des défauts ponctuels qui piègent la phase de l'ODC. Ce piégeage augmente la contrainte dans l'ODC et des défauts de l'ODC apparaissent. Dans 1T-TaS₂ les ODC incommensurables sont plus souples que celles commensurables dans 1T-TaSe₂ et des dislocations de l'ODC se créent plus facilement.

Abstract. — The formation of defects in the structural modulation associated with charge density waves (CDW) has been studied by electron microscopy in 1T-TaS₂ and 1T-TaSe₂. The irradiation with electrons creates lattice defects that pin the phase of the CDW. This pinning induces strain in the CDW and forms the CDW defects. The response of the commensurate CDW in 1T-TaSe₂ is more rigid with respect to the incommensurate 1T-TaS₂ CDW in which the CDW dislocations are much easierly formed.

1. Introduction.

Materials with modulated structures offer a wide range of interest for research in solid state physics. The multiple phase transitions and the occurrence of incommensurate and commensurate phases have been intensively studied in various physical systems [1].

In real materials all these phenomena are perturbed by the existence of defects and impurities. In this paper we shall present electron microscopy evidence of such perturbations in the charge density wave (CDW) modulated phases of the layer compound 1T-TaS₂ and 1T-TaSe₂. The present study extends the earlier observations which have already shown the important role of defects in the CDW materials [2].

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We shall present results on two distinct but rather similar CDW structures. The first is the incommensurate phase of 1T-TaS₂, the other the commensurate CDW phase of 1T-TaSe₂. In both materials, we introduce lattice defects (vacancies, interstitials) in a controlled way by irradiation in a high voltage electron microscope [3, 4]. Subsequent electron microscopy observations of both satellite reflection dark field images and high resolution images reveal the perturbations induced by these lattice defects in the structural modulation associated with the CDW. We shall limit ourselves to some room temperature observations that give a comparison of the effects of defects in the incommensurate phases.

2. CDW in 1T-TaS₂ and 1T-TaSe₂.

In 1T-TaS₂ and 1T-TaSe₂ the driving force of the charge density wave (CDW, a periodic modulation of the density of conduction electrons and of the atomic positions) is the instability of the quasi-two-dimensional electron gas [5]. Indeed, such a system is unstable with respect to a periodic perturbation with a wave vector $2k_F$, twice the Fermi wave vector of the conduction electrons [6]. A modulated structure is stable in both compounds up to at least 600 K. At room temperature, where we have our observations, the 1T-TaS₂ has a nearly commensurate (but definitely incommensurate) modulation, specific to this material [5, 7, 8]. In 1T-TaSe₂, the modulation is commensurate around room temperature. Energetically the two structures are closely related : the enthalpies of transition from a similar incommensurate phase are 123 cal/mol for 1T-TaS₂ at ~ 350 K and 338 cal/mol for 1T-TaSe₂ at ~ 470 K [5]. One might hence expect them to have a very similar response to foreign defect potentials. This is indeed true so far as the phase stability is concerned [3], but not the microscopic structural response, as will be shown below.

Transmission electron microscope is a very convenient tool for studying the CDW in 1T-TaS₂ and 1T-TaSe₂. The crystals can be easily cleaved along the weakly bound layers to obtain thin samples ($\lesssim 1\,000$ Å) that are transparent to the electron beam in the direction perpendicular to the layers of the structure. Electron diffraction reveals the satellite reflections associated with the CDW modulation. These reflected beams are strong enough for either dark field images (with a single reflected beam) or high resolution interference images (together with a main reflection) to be obtained [9]. In the first case we obtain relatively low magnification ($\simeq 50\,000$) images that show the overall coherence of the single modulation component. In the second case, we can discern fringes with the primitive periodicity of the CDW modulation, and distinguish perturbations at this length scale, i.e. about 9 Å in 1T-TaS₂ and 1T-TaSe₂. These two imaging methods are very powerful for the study of the microstructure of the CDW and we have used both of them for the observation reported below.

3. CDW defects in the commensurate 1T-TaSe₂.

Figure 1 shows the evolution of the satellite-reflection dark-field images after different irradiation doses, expressed in dpTa (displacement per Ta, i.e. the fraction of Ta atoms displaced by irradiation). In the non-irradiated material, figure 1a, we can see coherent commensurate domains separated by well defined boundaries that do not have any preferential crystallographic direction. The introduction of 2×10^{-3} defects (Fig. 1b) destroys the regular contours of the boundaries, and after 6×10^{-3} defects (Fig. 1c) it is possible to observe spot contrasts, localized defects in the CDW modulation. These point contrasts are dislocations of the CDW as it has been shown in high resolution electron microscopy observations [10]. Finally the density of dislocations becomes so high that a granular contrast is observed everywhere (Fig. 1d).

4. CDW defects in the nearly commensurate 1T-TaS₂.

An obvious difference between the dark field micrographs of 1T-TaS₂ is that no clearly distinguishable domain structure emerges (Fig. 2a). The dislocation point contrasts however, are

Fig. 1a-d. — The evolution of the satellite reflection dark field micrographs of 1T-TaSe₂ under irradiation with 2 MeV electrons. Note the irregularity of the domain boundaries in (b), the point contrasts of the defect on (c).

frequently observed even in the as grown material. The number of these CDW defects increases rapidly with increasing concentration of irradiation defects, as can be seen on figure 2b, c. Even though the form of the contrast is more irregular than the point contrast of the first reported observation [10], we can say that they are dislocations type defects. This is confirmed by the high resolution image of figure 3. The different forms of contrast are most probably related to different orientations of dislocations, a point is observed only when the dislocation occurs perpendicularly to the image plane.

Fig. 2a-c. — As in figure 1, for 1T-TaS₂. The defects observed as dark contrasts are CDW dislocations as it can be seen on the high resolution image of figure 3.

Fig. 3. — A tilted CDW dislocation in 1T-TaS₂. The Burgers circuit shows that there is one CDW period more in the upper part of the figure. Compare with the figure in reference [10].

5. Concluding remarks.

The formation of defects in the CDW modulation when lattice defects are introduced in the material can be understood as being due to the pinning of the CDW by defects [11, 12]. The CDW is pinned because its phase has a preferred value on the defect site. Consequently a random distribution of defects creates a frustrated situation, the preferred phase value cannot be obtained at all defect sites in the case of a rigid CDW. Only by elastic deformation of the CDW is it possible to gain some of the pinning energy [11, 12]; were the defects mobile, this might also be accomplished by allowing a short range migration of defects [13].

In the materials we have observed it is clear that the CDW is strained. In addition the strain has different consequences depending on whether the CDW is commensurate or not. Commensurate CDW are known to be rigid, their elastic deformation costs a finite amount of energy even for very long range deformation [14]. Accordingly we see the CDW broken in domains whose boundaries are the most easily deformable regions as we have observed. The incommensurate CDW, on the contrary, can be deformed at long range with minimal cost of energy [14] and there are no domains. On the other hand the strain due to pinning of the CDW can even exceed the elastic limit and we then observe the formation of dislocations in the CDW. The formation of dislocations is easy in the incommensurate CDW, the dislocation density is about $100 \mu\text{m}^{-2}$ at a defect concentration of 3×10^{-3} dpTa. In the commensurate 1T-TaSe₂ the first dislocations appears at defect concentrations approaching 10^{-2} dpTa.

References

- [1] COWLEY, J. M., COHEN, J. B., SALAMON, M. B. and WUENSCH, B. J., *Modulated Structures* (AIP Conference Proceeding, n° 53, American Institute of Physics, New York), 1979.
- [2] MUTKA, H., BOUFFARD, S. and ZUPPIROLI, L., *Conference on Charge Density Waves in Solids*, Proceeding Budapest, ed. by Gy. Hutiroy and J. Solyom (Springer-Verlag) 1984, p. 55.
- [3] SALVETTI, G., Thesis, Toulouse, France (1984).
- [4] MUTKA, H., Thesis, Orsay, France (1982).
- [5] WILSON, J. A., DI SALVO, F. J. and MAHAJAN, S., *Adv. Phys.* **24** (1975) 117.
- [6] FRIEND, R. H. and JEROME, D., *J. Phys. C* **12** (1979) 1441.
- [7] BROUWER, R., Thesis, Groningen, the Netherlands (1978).
- [8] BROUWER, R. and JELLINEK, F., *Physica B* **99** (1980) 51.
- [9] VAN LANDUYT, J., *Physica B* **99** (1980) 12.
- [10] SALVETTI, G., ROUCAU, C., AYROLES, R., MUTKA, H. and MOLINIE, P., *C. R. Hebd. Séan. Acad. Sci. Paris, Sér. II* **299** (1984) 843.
- [11] FUKUYAMA, H. and LEE, P. A., *Phys. Rev. B* **17** (1978) 535.
- [12] LEE, P. A. and RICE, J. M., *Phys. Rev. B* **19** (1979) 3970.
- [13] LEDERER, P., MONTAMBAUX, G., JAMET, J. P. and CHAUVIN, M., *J. Physique Lett.* **45** (1984) L-627.
- [14] In the Commensurate CDW the long range deformation of the phase phason excitations in the CDW dynamics are optical modes with finite energy at $k = 0$. In incommensurate CDW the phason energy goes to zero at long wavelength limit. See e.g. BRUCE, A. D., COWLEY, R. A., *J. Phys. C* **11** (1978) 3609.