LT-structural changes of the $(\text{NbSe}_4)_{10}\text{I}_3$ compound, a quasi-one dimensional charge density wave system

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Abstract

In order to study the structural background of the giant thermal hysteresis observed in the thermopower measurements [1] of the CDW system $(\text{NbSe}_4)_{10}\text{I}_3$, zeroth-order Weissenberg and oscillation photographs were taken at temperatures below Peierls transition. A reversible transformation of the room temperature tetragonal lattice into four symmetrically equivalent monoclinic domains was observed with the monoclinic angle behaving like an order parameter.

Introduction

More than ten years ago a series of new quasi-one-dimensional compounds with general formula $(\text{MSe}_4)_x\text{I}$; $\text{M}=\text{Ta}, \text{Nb}$; $x=2, 3, 10/3$ has been synthesized [2,3]. At room temperatures all of them have tetragonal symmetry but different space groups (I422, P4/mnc, P4/mcc, respectively). The common structural feature is an array of parallel well separated chains of metal atoms. The chains are at positions $(0, 1/2, z)$ and $(1/2, 0, z)$. Each metal atom is sandwiched between two Se_4 rectangular units rotated to each other by 45 degrees. There are also parallel rows of iodine atoms. The rows are at positions $(0, 0, z)$ and $(1/2, 1/2, z)$. Apart from the length of the c axis being 4, 6 and 10 metal-metal distances long for the 2/1, 3/1 and 10/3 compounds, respectively, the main structural differences come from distribution of iodine atoms within rows and their numbers per unit cell. In the case of 2/1 and 3/1 compounds all parallel iodine rows are equivalent having 2 iodine atoms per row. In the 10/3 case the rows at $(0, 0, z)$ contain 4 atoms while the rows at $(1/2, 1/2, z)$ contain 2 atoms thus forming the anisotropic iodine surrounding of each metal chain.

In two (2/1 and 10/3) of three compounds, CDW phenomena are observed below Peierls transition (260K and 285K, respectively) associated with nonlinear conductivity, switching, narrow-band noise and metastability [3,4]. For both CDW systems the components of $2k_F$ distortion wave vectors are observed as predicted from the electronic band-subband consideration [5,6]. They are $(\pm 0.05, \pm 0.05, \pm 0.085)$ [8] and $(0, 0, \pm 0.487)$ for 2/1 and 10/3 compound, respectively.

Regarding the metastability, a huge hysteresis has been recently found in thermopower vs. temperature experiments on 10/3 compound [1]. In order to search for the structural background of

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this hysteresis the single-crystal x-ray diffraction patterns of 10/3 compound were collected using Weissenberg and oscillation methods from room temperature down to 130K.

Experimental details

Two single crystals of $10 \times 10 \times 20 \mu\text{m}$ were selected from the same batch and glued to the goniometer head with a axis aligned along the oscillation axis. The standard low-temperature Enraf-Nonius Weissenberg camera is used with $\text{CuK}\alpha$ graphite-monochromated radiation and zeroth-layer $0kl$ Weissenberg and oscillation photographs were taken at different temperatures. The crystal was cooled by regulated and previously calibrated LN_2 vapour stream.

Results and discussion

Weissenberg and oscillation photographs taken below Peierls transition ($T_p = 280\text{K}$) have shown that Bragg spots of room temperature tetragonal phase with $l \neq 0$ are split, as a function of temperature, into 4 symmetrically equivalent spots of almost the same intensity. The indexes of the new Bragg spots in the tetragonal reference frame are: $(h + \eta_f(T), k, l)$, $(h - \eta_f(T), k, l)$, $(h, k + \eta_f(T), l)$ and $(h, k - \eta_f(T), l)$. The magnitude of splitting $\eta_f(T)$ continuously changes from zero at $T_p = 280\text{K}$ up to $0.011l$ at 130K . The splitting process is reversible with temperature. The splitting

measured in Weissenberg photographs gives directly the angle between two-by-two new c^* axes schematically shown in Fig.1. Since we deal with the four new sets of Bragg spots instead of single tetragonal one the conversion to real space is straightforward. At T_p there is a transformation of the tetragonal lattice into four symmetrically equivalent monoclinic lattice domains related to each other by the rotation around the fourfold axis. The monoclinic angle is a temperature dependent parameter changing from 90 degrees at T_p up to the 92.1 degrees at 130K . Since there is no splitting of the spots laying in the a^*, b^* plane ($l=0$) the monoclinic deformation of the tetragonal lattice is the consequence of the relative shift of the

Fig.1: Schematic presentation of the Bragg splitting below Peierls transition (T_p). $T > T_p$: tetragonal reciprocal lattice, $T < T_p$: one of four monoclinic domains reciprocal lattice.

neighbouring chains along the chain direction, i.e. 'transverse shear mode'. More precisely, there is a shearing of neighbouring planes parallel either to the a,c planes or to the b,c planes.

The temperature dependence of the monoclinic angle (β_M) in the cooling-heating cycle is shown in Fig. 2. Apart from Peierls transition there are two more anomalies: one at 220K and the other slightly below 200K. The temperature dependence of β_M resembles the order parameter behaviour

Fig.2: Variation of the monoclinic angle with temperature: cooling (o), heating (+). Full line is the sum of 3 critical dependences: $\beta_M \propto (T_{ci} - T)^{1/2}$; $T_{c1}=279.60\text{K}$, $T_{c2}=219.44\text{K}$, $T_{c3}=195.53\text{K}$.

with the critical exponent being roughly 0.50 ± 0.05 . The full line in Fig. 2 is the mean-field order parameter fit with three different independent critical temperatures keeping fixed the value of the critical exponent of $1/2$. In the region between 280K and 220K the obtained critical dependence is $(\beta_M - 90)_1 = 0.076 \times (279.60 - T)^{1/2}$. It is then subtracted from the measured values in the next region. The procedure is repeated in the temperature region between 220K and 200K and finally between 200K and 130K. The last two steps have revealed two more relations: $(\beta_M - 90)_2 = 0.070 \times (219.44 - T)^{1/2}$ and $(\beta_M - 90)_3 = 0.078 \times (195.53 - T)^{1/2}$. The values of coefficients should not be taken too strictly because of the limited precision of the measured data.

The obtained critical temperatures of 220K and 195K coincide with the temperatures of anomalies observed in transport measurements. Namely, 220K is the temperature at which in the threshold field vs. temperature dependence the termination of the hysteresis and the change of slope is observed [4]. The other characteristic temperature 195K coincides well with the maximum in the thermopower vs. temperature measurement [1].

Although one might notice similarity between the splitting observed in this work for 10/3 compound and that observed for the $(\text{TaSe}_4)_2\text{I}$ compound [8] the differences seem to be more instructive. Apart from $2k_f$ distortion wave vectors which are at different points in the Brillouine zone, i.e. near to the center and near to the edge of the zone for the 2/1 and 10/3 compounds, respectively, there are a few more important distinctions. First, domains observed in 2/1 compound are the periodic-lattice-distortion (PLD) domains having a common Bragg tetragonal lattice. Here in the case of 10/3 compound the domains are completely of Bragg type. Second, a^* and b^* components of the PLD wave vector in the case of 2/1 compound are temperature independent. In the case of 10/3 compound Bragg spot indexes h or k are critically dependent on temperature suggesting shear stress as an additional order parameter. Third, different splitting directions ($\pm a^* \pm b^*$) in the case of 2/1 and $\pm a^*$ or $\pm b^*$ in the case of 10/3 compound) are probably due to the second-neighbours interchain interaction anisotropy, pointing to the critical importance of details of CDW interchain interactions.

It is also worth noting that at room temperature a strong diffuse scattering around all spots except those having $l=0$ is observed. Although not examined in detail, it may be described as being perpendicular to c^* direction and extended over the whole Brillouine zone, modulated by the intensity of the parent spot. It is not clear whether it comes from a certain iodine ions disorder in the rows [2] or that its origin lays in X-ray diffraction on low-energy phonons. If the scattering on phonons is the underlying mechanism then these are TA phonons having wave vectors' directions in the a,b plane and polarization vector along the chain direction. This might explain the origin of transverse shear mode in the LT-phase if a coupling to the $2k_f$ distortion wave vector exists.

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