

Thermal hysteresis in thermopower of the charge-density-wave system $(\text{NbSe}_4)_10\text{I}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 3273

(<http://iopscience.iop.org/0953-8984/4/12/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 11:37

Please note that [terms and conditions apply](#).

Thermal hysteresis in thermopower of the charge-density-wave system $(\text{NbSe}_4)_{10}\text{I}_3$

A Smontara†, K Biljaković†, J Mazuer†, P Monceau‡ and F Lévy§

† Institute of Physics of the University, 41001 Zagreb, PO Box 304, Croatia

‡ Centre de Recherches sur les Très Basses Températures, CNRS BP 166X, 38042 Grenoble Cédex, France

§ Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Received 11 September 1991, in final form 30 December 1991

Abstract. Measurements of the thermopower in the charge density wave compound $(\text{NbSe}_4)_{10}\text{I}_3$ show a large hysteresis between the cooling and heating cycles below and above the Peierls transition temperature. The magnitude of the observed hysteresis depends on the lowest temperature reached in the cooling regime. This effect is attributed to the interaction between charge density wave deformations and a quasi-periodic structure of lattice defects.

1. Introduction

Quasi-one-dimensional systems exhibiting a Peierls transition with the concomitant formation of a charge density wave (CDW) and a lattice distortion, such as transition metal trichalcogenides NbSe_3 , NbS_3 , TaS_3 , ... molybdenum oxides $\text{K}_{0.3}\text{MoO}_3$, halogenated transition metal tetrachalcogenides $(\text{TaSe}_4)\text{I}$, $(\text{NbSe}_4)_2\text{I}$, $(\text{NbSe}_4)_{10}\text{I}_3$, ... have aroused much interest in recent years essentially because of spectacular non-linear transport properties associated with the moving CDW condensate (for a review see Monceau 1985, Rouxel 1986, Schlenker 1989, Gor'kov and Grüner 1989). However, the nature of the phase transition—weak electron–phonon coupling versus strong coupling with a possible bipolaronic CDW ground state (Aubry and Quémenerais 1989), displacive versus order–disorder type (Pouget 1989) still remains largely unsettled. Thermodynamic and transport properties in the linear state of many Peierls conductors have revealed anomalous behaviour with respect to the mean-field BCS type theory: then the gap amplitude measured from the activated variation of the conductivity deviates strongly from the classical 3.5 value with, typically, $2\Delta(0)/kT_p$ between 8 and 12 (Monceau 1985), the specific heat anomaly at T_p is much larger than predicted in the mean field theory (Kwok *et al* 1990), the thermal conductivity shows also a peak at T_p which is at variance with what is expected from a smooth lattice and electronic contribution in the vicinity of T_p (Smontara *et al* 1989b, Kwok and Brown 1989). The CDW density is defined as $\rho(r) = \rho_0 + \rho_1 \cos |Qr + \Phi(r)|$ with the CDW wave vector $Q = 2k_F = 2\pi/\lambda$ (λ is the CDW wavelength) and $\Phi(r)$ the phase with respect to the ionic structure. Because of the interaction with impurities, the phase Φ is pinned and may freeze Q at a non-equilibrium average value. Consequently, hysteresis appears in the low-field conductivity when T is cycled up and down

(Higgs and Gill 1983). This effect is stronger in systems in which Q is temperature-dependent as in TaS_3 (Mihály and Mihály 1984, Wang and Ong 1986) and $\text{K}_{0.3}\text{MoO}_3$ (Fleming and Schneemeyer 1983, Wang and Ong 1987). These metastable states may slowly relax to equilibrium with a very large spread in the time constant depending on temperature and also on the application of an electric field. In such a case a variation of the normal resistance following a $\log t$ law has been reported (Mihály and Mihály 1984). These metastable states have also been shown to manifest themselves in the specific heat at very low temperatures ($T < 0.5$ K) yielding a larger contribution than that due to phonons in T^ν with $\nu < 1$ (Lasjaunias *et al* 1990) and to exhibit ageing effects in energy relaxation similar to spin glasses (Biljaković *et al* 1989).

In this respect thermopower (TEP) is a particularly interesting transport property because it is a very sensitive probe of the carrier balance, of the relative rate of phonon-phonon and carrier-phonon interactions and of the Fermi surface. In so far as they reflect the disordered CDW ground state, the equilibrium time scales greatly exceed practical time scales, and so in practical conditions of measurement the equilibrium value of the TEP will not be reached and thermal hysteresis will be observed. In this paper we describe a detailed investigation of the temperature dependence of TEP for the CDW system $(\text{NbSe}_4)_{10}\text{I}_3$. In contrast with recent work (Bansal and Surendranath 1990) our results reveal a large thermal hysteresis between different temperature cycles as well as time dependence. Preliminary observation of the hysteresis in TEP was reported by Smontara *et al* (1989a).

2. Experimental procedure

$(\text{NbSe}_4)_{10}\text{I}_3$ belongs to the $(\text{MX}_4)_n\text{I}$ family (with $M = \text{Ta}, \text{Nb}$). These compounds consist of MX_4 parallel chains separated by iodine. In each chain the niobium atom is located at the centre of a rectangular antiprism of eight selenium atoms. The filling of the d_z band of each niobium is given by $(n-1)/2n$ (Gressier *et al* 1984b). This incomplete band filling is favourable to a Peierls distortion. Such a transition has been detected in $(\text{TaSe}_4)_2\text{I}$ at $T_p = 263$ K (Wang *et al* 1983b) and $(\text{NbSe}_4)_{10}\text{I}_3$ at $T_p = 285$ K (Wang *et al* 1984b), while in $(\text{NbSe}_4)_3\text{I}$ a ferrodistorive transition occurs at 273 K (Gressier *et al* 1984a). The analyses of the NMR line shapes have shown that the CDW in $(\text{NbSe}_4)_{10}\text{I}_3$ is incommensurate (Butaud *et al* 1985). NMR measurements have also yielded the temperature dependence of the CDW order parameter. Satellite spots have been observed below T_p in $(\text{NbSe}_4)_{10}\text{I}_3$ which allows the determination of the Q vector of the CDW as $(0, 0, 0.487c^*)$ at $T = 100$ K (Roucau *et al* 1984). Furthermore, high-resolution images from electron microscopy have revealed interference fringes corresponding to the atomic planes perpendicular to the c axis with the periodicity $c = 31.9$ Å disturbed by the existence of 'fault planes' with periodicity roughly equal to $11c$. In fact the sequence of 'fault planes' is complex: images have revealed periodic sequences $9c + 12c + 10c + 9c + 12c = 52c = 1660$ Å. These plane defects are independent of temperature, at least between 100 K and 400 K (Roucau and Ayrolles 1985). Along the c axis the niobium atoms have the repeat distance of 5 units with Nb-Nb distances (Å) of 3.17, 3.17, 3.23, 3.15, 3.23. However, the c parameter comprises 10 niobium atoms because of the unequivalent channels $(0, 0, z)$ and $(1/2, 1/2, z)$ for iodine atoms (Meerschaut *et al* 1977). Because of the unequivalent Nb-Nb distances, the electrical resistivity is rather large, typically $150 \mu\Omega$ m at room temperature (Wang *et al* 1983a). The Hall constant R_H is positive

indicating hole-like carriers with a density of $0.7 \times 10^{21} \text{cm}^{-3}$ in agreement with band calculations if the d band of the niobium is only folded in five sub-bands as proposed by Petravić *et al* (1989).

TEP measurements have been independently performed on three different crystals using two methods. The first was a standard temperature-gradient technique between room temperature and liquid-nitrogen temperature. The samples were mounted on two small, electrically insulated copper thermal reservoirs. Electrical connections to the sample were made via annealed gold leads attached to its ends using gold paint. The temperature difference on the sample was measured by means of a differential Au(0.03% Fe)–chromel thermocouple with junctions glued by General Electric varnish as close as possible to the electrical connection for measuring the TEP. At each temperature we reversed the temperature difference on the sample several times keeping it lower than 1 K. The experimental set-up was checked by measuring a piece of lead wire. A detailed investigation of the TEP of tetrachalcogenides with different cycling conditions especially in the case of $(\text{NbSe}_4)_{10}\text{I}_3$ has been performed previously using this method (Smontara *et al* 1989a).

Since we wanted to see if similar hysteretic effects in other physical properties exist, we also used a second method which allows simultaneous measurements of TEP, thermal conductivity and electrical resistivity (Chaussy *et al* 1981). In this case the sample was placed in a calorimeter under vacuum, this being necessary for thermal conductivity measurements. It was electrically and thermally connected at one end to the sample holder and at the other end to the heater by silver paste. The resistivity of the sample was measured under isothermal conditions before the temperature gradient $\Delta T/\Delta x$ was applied. Two thermocouples AuFe0.07% and chromel were used to determine the TEP of the sample, so that it was not necessary to know the temperature gradient ($\Delta T/T < 1\text{--}2\%$). The effective dimensions of the sample used in this method were $1.5 \times 0.35 \text{mm}^2$. The contacts were made by evaporating gold, and the thermocouple wires were attached to them with silver paste. The TEP measurements together with electrical resistivity and thermal conductivity were performed in the temperature region from 1 K to 350 K with very slow cooling (warming) rates of a few K per hour, even less than 1K h^{-1} in the region of the Peierls transition.

3. Results

Variation of the low-field resistivity of $(\text{NbSe}_4)_{10}\text{I}_3$ together with its logarithmic derivative as a function of the inverse of the temperature is shown in figure 1. For this sample (sample 1) the room-temperature value of the chain-axis resistivity is $\rho_{\text{RT}} = 110 \mu\Omega\text{m}$, $T_p = (279 \pm 1) \text{K}$ and the well-defined low temperature energy gap $E_g(0) = 3720 \text{K}$ in good agreement with the previous results of Wang *et al* (1983a). The accuracy of the resistivity measurements performed with a low-frequency bridge (33 Hz) was 0.1% so that we were able to detect a small hysteresis as shown in the inset of figure 1 and also previously reported by Petravić *et al* (1989). The resistivity in the heating cycle was up to 2% greater than the one in the cooling cycle at temperatures around 200 K. The width of this hysteresis increased up to 5–6% at 140 K. The TEP measured on the same sample, as shown in figure 2 is positive down to approximately 150 K with a change of behaviour from semi-metallic to semi-conducting as the CDW gap opens at T_p . There is a maximum in the TEP

when cooling down at $T_m = 220$ K and a much larger one after heating, the height and position of which depends on the lowest temperature reached in the cycling. Below $T_0 = 160$ K the TEP changes sign, going to a minimum, and remains negative down to the lowest temperatures, slowly approaching the zero value. We measured the temperature dependence of the TEP in heating for different samples and found it to be in qualitative agreement with the results of Bansal and Surendranath (1990). However, these authors did not mention any hysteresis, so it is very likely their measurements were only performed in the heating regime. The absolute values found by Bansal and Surendranath (1990) correspond more closely to those of sample 2 which we measured using the first method as shown in figure 3. This sample was the same one as had been used for Hall-effect measurements by Petrávič et al (1989).

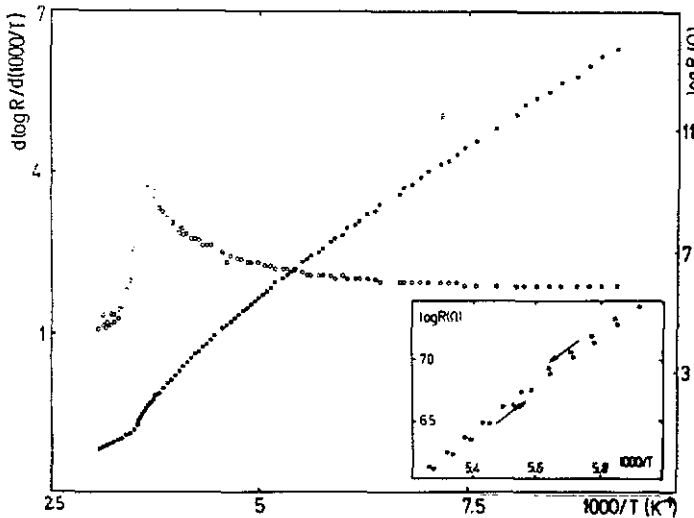


Figure 1. Variation of the low-field resistivity together with its logarithmic derivative of $(\text{NbSe}_4)_{10}\text{I}_3$ as a function of inverse temperature ($1000/T$) for sample 1. The inset shows a hysteresis of a few percent below 200 K.

To our knowledge, hysteresis in the TEP as great as that shown in figures 2 and 3 has never been reported before. The maximum hysteresis loop is obtained when the sample is cooled below 100 K. In figure 2 we show the temperature variation of the TEP when the sample is cooled to 80 K and warmed, and cooled to 4.2 K and warmed. There is no further effect on the hysteresis loop after cooling at temperatures lower than 70 K. More detailed information on the hysteresis in the TEP is shown in figure 3 with different cycling temperatures, which show that the envelope of each hysteresis loop is formed through extreme temperature cycling. When cooling down only to 200 K (point A), and then heating, the TEP follows the trajectory A-B reaching the major hysteresis loop. On the other hand if on heating the temperature is reversed (cooling) before it reaches room temperature (points C, D, E) the TEP decreases and reaches the lower part of the major hysteresis loop. It can also be seen in figure 2 that hysteresis also occurs above T_p but with opposite variation in temperature with respect to that below T_p : i.e. the TEP is larger when T is reduced. At room temperature the width of the hysteresis loop is 20% of the average TEP value. In this case there is a node in the hysteresis behaviour at $T \sim 262$ K, 20 K lower than T_p . Since the maximum TEP below T_p occurs at different temperatures

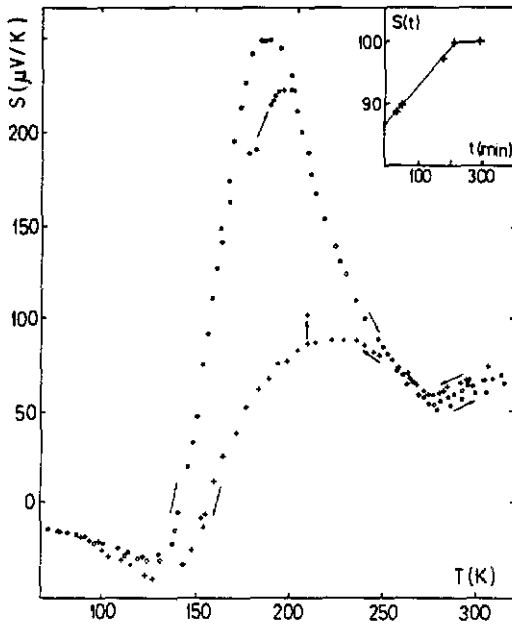


Figure 2. Thermopower of sample 1 versus temperature. Data obtained in the cooling regime are represented by crosses (+) and the data in the heating regime by circles: empty circles (O) after cooling down to 80 K and full circles (●) after cooling down to 4.2 K. In the inset is the time dependence of the TEP at 210 K indicated by an arrow in the figure.

on the heating and cooling curves, so similarly, the minimum TEP in the vicinity of T_p occurs 5 K lower in cooling than in heating above room temperature. Further experiments are in progress to determine the (maximum) temperature at which the hysteresis loop vanishes.

Finally, preliminary measurements have revealed the time dependence of the TEP as shown in the inset of figure 2. On the heating cycle when T is stabilized at $T = 210$ K, the TEP increases from $87 \mu\text{V K}^{-1}$ to $100 \mu\text{V K}^{-1}$ as a function of time. The measurements of the rate of this variation as a function of temperature are also in progress.

4. Discussion and conclusions

The thermopower is the energy measured relatively to the Fermi energy carried by electrons or holes per unit charge divided by the temperature. For an uncorrelated degenerate Fermi gas, the thermopower S and the conductivity σ are derived from the Boltzmann equation (Ziman 1972, Chaikin *et al* 1976)

$$S = -K_1 / |e|TK_0 \tag{1}$$

$$\sigma = e^2 K_0 \tag{2}$$

K_0, K_1 are the generalized transport coefficients given by

$$K_n = -\frac{1}{3} \int v_k^2 \tau_k (\epsilon_k - \mu)^n \frac{\partial f^0(k)}{\partial \epsilon_k} d^3k \tag{3}$$

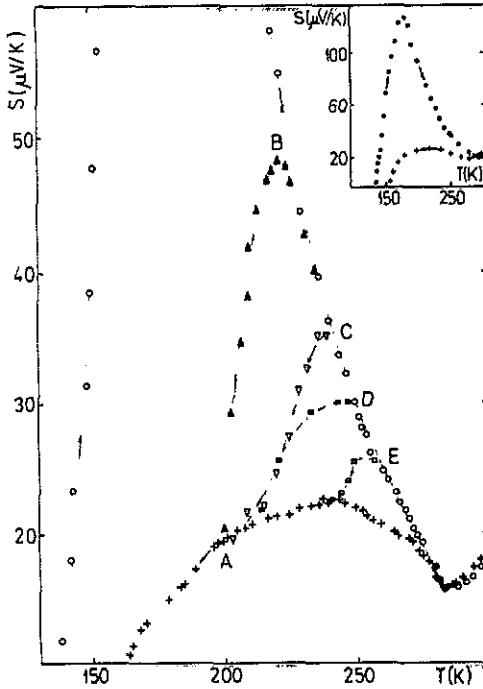


Figure 3. The thermopower of sample 2 shows different hysteric loops when the heating has been stopped at different points of the maximum, and the sample then cooled down again. The extreme hysteric loop in the cooling regime (+), and in heating after cooling down to 80 K (O) is shown in inset. Path AB—data when cooling is stopped at A and warmed again; points C, D, E—when the heating is stopped at a different temperature and the sample cooled again.

with v_k the band velocity, τ_k the scattering time, ε_k the energy, μ the chemical potential, and $f^0(k)$ the Fermi-Dirac distribution function. Analytic expression of S can be derived with simplifying assumptions about the band shape, the scattering times and the type of carriers; then for free electrons in the metallic state, S varies linearly with T with the slope $\pi^2 k^2 / |e| E_F$. While S in $(\text{NbSe}_4)_{10}\text{I}_3$ shows a linear T dependence above T_p , it is, however, risky to derive E_F from this measurement; indeed the temperature range is relatively restricted and, furthermore, one expects CDW fluctuation contributions above T_p which should alter the canonical expression for the metallic state. For intrinsic semiconductors, S is essentially dependent of $E_g/2kT$ where E_g is the energy gap but normalized by a function of the rates of electron to hole mobility (Fritzsche 1971). The TEP data shown in figure 2 have been redrawn in figure 4 as a function of $1/T$. In the temperature range in which the cooling and heating cycles are joined, one can define an effective gap of ≈ 2000 K, lower than the value of 3720 K deduced from resistivity measurements indicating a large asymmetry in electron and hole mobility in $(\text{NbSe}_4)_{10}\text{I}_3$ as already noticed by Bansal and Surendranath (1990). In the interpretation of the experimental Hall data the problem of the electron-hole asymmetry has been discussed by Petravić *et al* (1989). This electron-hole asymmetry has been recently shown to result from the curvature of ε_k near E_F (the usual description of the 1D electron gas is to linearize ε_k near E_F) which yields a variation of the Fermi level position with respect to the

mid-gap energy and a variation of the wave vector Q with T (Noguera and Pouget 1991). The temperature dependence of Q has been measured in TaS_3 (Monceau 1985), $\text{K}_{0.3}\text{MoO}_3$ (Schlenker 1989) and also recently in NbSe_3 (Moudden *et al* 1990). Unfortunately, however, the Q vector in $(\text{NbSe}_4)_{10}\text{I}_3$ has only been measured at 100 K and the search of the temperature dependence of the CDW wave vector in this compound is highly desirable.

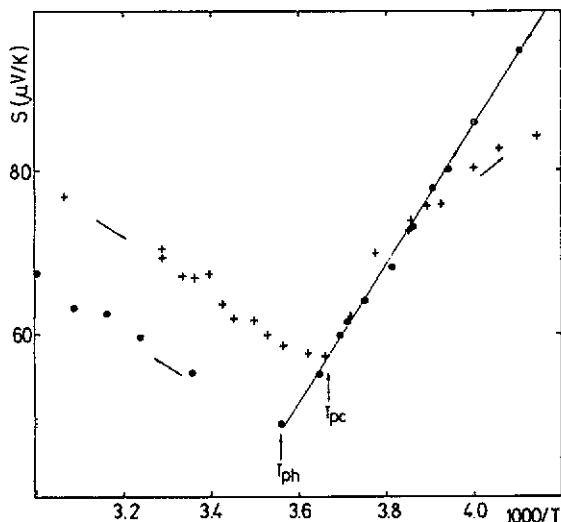


Figure 4. The thermopower of sample 1 as a function of inverse temperature in the vicinity of the Peierls transition with the same symbols as in figure 2. The line represents the best fit to the semiconducting behaviour.

The temperature dependence of $S(T)$ in $(\text{NbSe}_4)_{10}\text{I}_3$ has general features—essentially a pronounced peak below T_p —similar to that in other CDW compounds as $(\text{TaSe}_4)_2\text{I}$ (Smontara *et al* 1989b), TaS_3 (Johnston *et al* 1983, Higgs 1985). It has been argued that the observed TEP peak at 180 K originates from phonon-drag effects (Bansal and Surendranath 1990). In classical semiconductors (and also in metals and alloys) the phonon drag is generally observed at T well below the Debye temperature θ_D . This temperature is not known exactly for $(\text{NbSe}_4)_{10}\text{I}_3$ but it is not expected to be very different from the values for similar compounds such as $(\text{NbSe}_4)_3\text{I}$ or $(\text{TaSe}_4)_2\text{I}$, i.e. $\theta_D \sim 116$ K (Smontara 1991a) and ~ 124 K (Smontara *et al* 1991b) respectively, which are much lower than the maximum in the TEP and which rule out this type of interpretation. The increase in the TEP below T_p seems likely to be a Fermi-surface effect.

As explained in the introduction, the pinning of the phase of the CDW to impurities may freeze the wave vector to a non-equilibrium average value. There are an arbitrary number of CDW metastable states and the choice of a certain metastable state depends on the electrical and thermal history of the sample as well as the time scale of observation. With a slight change in T , especially when Q is temperature dependent, the system is sent into a state remote from the true equilibrium configuration with a possible relaxation into equilibrium. These metastable states yield the hysteresis in the temperature dependence of the resistivity as intensively studied in TaS_3 (Mihály *et al* 1984, Wang and Ong 1986). The metastable states have also been studied from the observation of the anomalous electromotive force (EMF) when a TaS_3 sample is

illuminated with a narrow laser beam (Itkis *et al* 1986). This EMF appears because the spatial distribution of residual deformation of the CDW and hysteresis depend on the way the beam is moved along the crystal. If the CDW vector Q is far away from the equilibrium, because of its interaction with impurities, a phase gradient will occur which means that additional charges with density $\delta\rho(x) \sim d\phi/dx$ will appear. The variation of $\phi(x)$ may be continuous but may also show a jump of π/m (discommensurations, or soliton for $m = 1$). The change in charge density due to an inhomogeneous distribution of the CDW induces a change in the chemical potential $\delta\mu \sim d\phi/dx$. The shift of chemical potential can be greatly increased if the density of quasi particles is small, and it is 5 times smaller in $(\text{NbSe}_4)_{10}\text{I}_3$ than in $(\text{TaSe}_4)_2\text{I}$ (Petračić *et al* 1989). Away from the centre of the gap, shifts of the chemical potential can be provided by phase gradient of both signs, i.e. additional charges can be positive or negative producing n-type or p-type doping in the crystal (Artemenko *et al* 1986). The thermopower is essentially sensitive to the position of the chemical potential and consequently will reflect this inhomogeneous CDW state.

Hysteresis with a weak amplitude (a few %) has been previously reported in TaS_3 (Higgs 1985) and in 2H-TaSe_2 (Gnanarajan and Frindt 1986) in the temperature range between the incommensurate CDW at 122 K and its locking to commensurability at 60 K. For this latter compound the hysteresis is related to the carrier-scattering effects associated with CDW commensurate and incommensurate domain walls. Small-amplitude hysteresis has been also recently measured in TEP of $\text{R}_{0.3}\text{MoO}_3$ and $\text{K}_{0.3}\text{MoO}_3$ in the temperature range where $q(T)$ reaches the low- T saturation near the commensurability value (Almeida *et al* 1991). Although the hysteresis in the TEP in $(\text{NbSe}_4)_{10}\text{I}_3$ is very large, TEP experiments on the parent compound $(\text{TaSe}_4)_2\text{I}$ have not revealed similar effects. One is then led to propose that the intrinsic inhomogeneity in this type of crystal is provided by the regular periodicity of the 'fault planes' as discussed in the experimental section of this paper. The defect lattice structure has a periodicity in the same range as the CDW wavelength ($\sim 4c$). This defect can strongly pin the CDW and produce CDW defects as solitons. The pinning force may be strongly hysteretic with temperature and consequently the phase gradient too. $(\text{NbSe}_4)_{10}\text{I}_3$ would then be a very interesting compound in which intrinsic periodic pinning on the CDW could be studied.

In conclusion we have shown that the temperature-dependent thermopower in the CDW compound $(\text{NbSe}_4)_{10}\text{I}_3$ is highly hysteretic with a node in the vicinity of the Peierls transition. The increase of the TEP below T_p is mainly a Fermi-surface effect. We propose that this large hysteresis results from the interaction between the inhomogeneous CDW superlattice and a quasi-periodic defect structure. Further experiments have to be performed as to the temperature dependence of the CDW wave vector, the search for the extreme temperature for the hysteresis of the loop above T_p and the time dependence of the TEP in the hysteresis regime.

Acknowledgments

We would like to thank L Forró for his help during the experimental work, to J R Cooper for his support and S N Artemenko and E Tutis for helpful discussion. One of us (AS) thanks all those at CRTBT, CNRS in Grénoble for their hospitality during her visit. This work is partially supported by research project No.Yu-ECC C11*0526-M(CD).

References

- Almeida M, Lopes E B and Dumas J 1991 *Synth. Met.* **41–43** 3833
- Artemenko S N, Volkov A F and Kruglov A N 1986 *Sov. Phys.-JETP* **63** 906
- Aubry S and Quémenerais P 1989 *Low-dimensional Electronic Properties of Molybdenum Bronzes and Oxides* ed C Schlenker (Dordrecht: Kluwer) p 295
- Bansal C and Surendranath K 1990 *Solid State Commun.* **76** 209
- Biljaković K, Lasjaunias J C, Monceau P and Lévy F 1989 *Phys. Rev. Lett.* **62** 1512
- Butaud P, Ségransan P, Berthier C and Meerschaut A 1985 *Springer Lecture Notes in Physics 217* ed G Hutiray and J Solyom (Berlin: Springer) p 121
- Chaikin P M, Greene R L, Etemad S and Engler E 1976 *Phys. Rev. B* **13** 1627
- Chaussy J, Guessous A and Mazuer J 1981 *Rev. Sci. Instrum.* **52** 1721
- Fleming R M and Schneemeyer L F 1983 *Phys. Rev. B* **28** 6996
- Fritzsche H 1971 *Solid State Commun.* **9** 1813
- Gnanarajan S and Frindt R F 1986 *Phys. Rev. B* **33** 1443
- Gor'kov L P and Grüner G 1989 *Charge Density Wave in Solids, Modern Problems in Condensed Matter* (Lausanne: Elsevier) p 15
- Gressier P, Meerschaut A, Guemas L, Rouxel J and Monceau P 1984a *J. Solid State Chem.* **51** 141
- Gressier P, Whangbo M H, Meerschaut A and Rouxel J 1984b *Inorg. Chem.* **23** 1221
- Higgs A W 1985 *Springer Lecture Notes in Physics 217* ed G Hutiray and J Solyom (Berlin: Springer) p 422
- Higgs A W and Gill J C 1983 *Solid State Commun.* **47** 737
- Itkis M E, Nad' F Ya and Pokrovskii V Ya 1986 *Sov. Phys.-JETP* **63** 177
- Johnston D C, Stokes J P, Hsieh P L and Grüner G 1983 *J. Physique Coll.* **44** C3 1749
- Kwok R S and Brown S E 1989 *Phys. Rev. Lett.* **63** 895
- Kwok R S, Grüner G, and Brown S F 1990 *Phys. Rev. Lett.* **65** 365
- Lasjaunias J C, Biljaković K and Monceau P 1990 *Physica B* **165 & 166** 893
- Meerschaut M, Palvadeau P and Rouxel J 1977 *J. Solid State Chem.* **20** 21
- Mihály G, Kriza G, and Jánossy A 1984 *Phys. Rev. B* **30** 3578
- Mihály G and Mihály L 1984 *Phys. Rev. Lett.* **52** 149
- Monceau P 1985 *Electronic Properties of Inorganic Quasi One-dimensional Compounds, Parts I and II* (Dordrecht: Reidel) Part I, p 41; Part II, p 139
- Moudden A H, Axe J D, Monceau P and Lévy F 1990 *Phys. Rev. Lett.* **65** 223
- Noguera C and Pouget J P 1991 *J. Physique I* **1** 1035
- Petavić M, Forró L, Cooper J R and Lévy F 1989 *Phys. Rev. B* **40** 2885
- Pouget J P 1989 *Low-dimensional Electronic Properties of Molybdenum Bronzes and Oxides* ed C Schlenker (Dordrecht: Kluwer) p 87
- Roucau C and Ayroles R 1985 *Springer Lecture Notes in Physics 217* ed G Hutiray and J Solyom (Berlin: Springer) p 65
- Roucau C, Ayroles R, Gressier P and Meerschaut A 1984 *J. Phys. C: Solid State Phys.* **17** 2993
- Rouxel J 1986 *Crystal Chemistry and Properties of Materials with Quasi One-dimensional Properties* (Dordrecht: Reidel) p 256
- Schlenker C 1989 *Low-dimensional Electronic Properties of Molybdenum Bronzes and Oxides* (Dordrecht: Kluwer) p 159
- Smontara A 1991a *PhD Thesis* University of Zagreb, Croatia (unpublished)
- Smontara A, Bihar Z and Biljaković K 1991b *Synthetic Metals* **43/3** 3981
- Smontara A, Biljaković K and Forró L 1989a *Fiz. Suppl.* **1** 123
- Smontara A, Biljaković K and Lévy F 1989b *Fiz. Suppl.* **3** 127
- Wang Z Z, Monceau P, Renard M, Gressier P, Guemas L and Rouxel J 1983a *Solid State Commun.* **47** 439
- Wang Z Z and Ong N P 1986 *Phys. Rev. B* **34** 5967
- 1987 *Phys. Rev. B* **35** 5896
- Wang Z Z, Saint-Lager M C, Monceau P, Renard M, Gressier P, Meerschaut A, Guemas L and Rouxel J 1983b *Solid State Commun.* **46** 325
- Ziman J M 1972 *Electrons and Phonons* (Oxford: Clarendon)