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Hysteresis and memory effects in irradiated potassium blue bronzes

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Résumé. — Les bronzes bleus de molybdène présentent à basse température des phénomènes dépendant du temps. Ces propriétés associées aux ondes de densité de charges sont sensibles à la présence de défauts. Nous présentons une étude du cycle d’hystérésis en température sur des échantillons dans lesquels les défauts sont introduits par irradiation. Nous montrons que les phénomènes observés sont amplifiés par la présence de défauts. Après une relaxation à température constante nous observons que les courbes résistance-température présentent un plateau interprété comme un piégeage du nombre de porteurs. Un effet mémoire est également décrit : le système se souvient au réchauffement de la température à laquelle la relaxation a été effectuée.

Abstract. — Molybdenum blue bronzes exhibit below the Peierls transition time-dependent phenomena. These properties, which are related to the charge density wave instability, are often associated to the presence of defects. In this paper we show that the hysteresis observed during temperature cycling is amplified when defects are introduced by irradiation. We describe two new phenomena observed after a constant temperature relaxation: on cooling the resistance versus temperature curves show a plateau attributed to a fixed number of carriers; on heating we observe a memory effect at the relaxation temperature.

Remarkable metastable phenomena showing hysteresis within a single phase and stretched exponential/logarithmic relaxations have been observed in many charge density wave (CDW) compounds [1-4]. The most striking examples of this behaviour have been encountered in the CDW phase of the blue bronzes and there is some evidence suggesting that the metastability is associated with the pinning of the CDW by lattice defects [4, 5]. Such a pinning is known to affect the collective CDW dynamics strongly: the threshold field of sliding CDW conductivity increases when defects are introduced at the ppm level by means of fast electron irradiation [6].

More generally, the idea of pinning by defects has been evoked to explain metastability, hysteresis and temporal relaxation in incommensurate phases of different origins (CDW [7], insulators [8-12], spin density waves [13]). Due to pinning, metastable out-of-equilibrium values of the order parameter or modulation wave vector for example, can be reached after changes of the thermodynamic variables [4, 14, 15]. Different kinds of memory effects are also commonly observed in presence of pinned incommensurate modulations [7, 9, 11]. Most of the experimental observations are included in the phenomenological defect density wave theory [11, 15] but there is actually little direct evidence of the role of defects in the phenomena listed above.

A close correlation between metastability and defect concentration in potassium blue bronze (K_{0.30}MoO_3) is a main result of the present work. In particular, irradiation experiments permit us to characterize a new thermal memory effect that is enhanced by defects. The results are discussed in the framework of recent ideas concerning the electronic band structure of the blue bronze which have been proposed to explain the thermal variation of the modulation wave vector q [16]. We obtain a consistent picture in which hysteresis and memory effects result from pinned out-of-equilibrium values of q.

1. Experimental methods.

The metastable CDW states were investigated by resistivity measurements using low field alternating excitation with amplitudes always well below the threshold of collective CDW conductivity. A classical
four probe configuration was used with contacts made by silver paste on evaporated gold stripes. The hysteresis $R(T)$ curves were measured while changing the temperature at a constant rate of the order of $3 \text{ K} \cdot \text{min}^{-1}$. The form of the hysteresis curve did not change with faster heating or cooling rate of at least up to $10 \text{ K} \cdot \text{min}^{-1}$.

Under the same conditions of temperature variation, we have also measured the Hall constant using an alternating electric current at frequency $f_0 \sim 1000 \text{ Hz}$ and an alternating magnetic field ($f_0 \sim 1180 \text{ Hz}$). The Hall voltage was detected by a lock-in amplifier at the frequency $f_1 - f_0$. This device which has the advantage to eliminate the contributions of the magnetoresistivity allows us to measure a Hall voltage of the order of $0.1 \mu\text{V}$ with a 400 gauss modulated field. The magnetic field was parallel to the (201) direction and the low ac excitation along the high conducting axis. For the Hall effect measurements we have used indium ultrasonic soldered probes.

Defects were produced in situ, at random positions, by irradiation with 2.5 MeV electrons as it has been reported earlier [5,6]. After low-temperature irradiations some samples were heated up to room temperature while some others were kept below 200 K. As demonstrated below, between these two temperatures some modifications of the defect number-configuration or sample aging were observed. The concentration of stable defects for a given irradiation dose was evaluated earlier by electron spin resonance measurement to be of the order of $10^{-5}$ atomic fraction for doses of $1 \text{ mC/cm}^2$ ($6.2 \times 10^{15} \text{ el/cm}^2$). All observations reported here were made with irradiation doses up to a few tens of mC/cm$^2$ when the effects on the average CDW amplitude are negligible but when the threshold field for non-linear conduction is shifted to a field greater than $10 \text{ V} \cdot \text{cm}^{-1}$ [6].

2. Results.

The $R(T)$ curves of non-irradiated blue bronze samples are known to possess a global hysteresis [1,3]. The extreme resistivity difference is typically of the order of 50% around 100 K, 80 degrees below the Peierls transition. The amplitude of this hysteresis increases up to a factor of two after an irradiation dose of a few tenths of mC/cm$^2$ as represented in figure 1. Superimposed to this effect a low-temperature decrease of the resistance is also observed, as it is usual in irradiated CDW compounds. The increase of the width of the hysteresis cycle shows that defect concentrations in the range of $10^{-4}$ atomic fraction can effectively increase the deviation from equilibrium of the CDW, as it was already observed in irradiated orthorhombic TaS$_3$ [17]. For the highest dose the out-of-equilibrium state is more and more frozen so that relaxation towards stable states becomes more and more difficult in the whole temperature range: thus the cycle closes again and becomes strongly dependent on the temperature variation rate. Nevertheless for doses lower than $50 \text{ mC/cm}^2$, provided that the temperature range is kept constant, typically between 40 and 200 K, the limiting $R(T)$ curves of the cycle are totally reproducible. However by restricting the temperature cycling below the Peierls transition temperature, new interesting phenomena occur.

Figure 2 shows an example of a thermal memory effect and a modified hysteresis that was observed on an irradiated sample after a relaxation of several hours at 90 K. After the relaxation, on cooling, we find a weakened temperature dependence of resistivity. On heating up towards the relaxation temperature a remarkable memory effect appears: a broad anomaly of the $R(T)$ curve can be seen. The heating curve turns down and tends to follow the slope of the cooling curve that started from the relaxation temperature. Similar anomalies can be observed in the non-irradiated samples too, but their amplitude is more than a factor of ten smaller both on temperature and resistivity scales. The memory effect, both in pure and irradiated samples, is best observed in the temperature range from about 65 to 120 K. Below this range, the slow relaxation makes it difficult to observe although it might exist. When the relaxation temperature goes above this range the memory effect gradually disap-
Fig. 2. — Resistance in a log scale as a function of the inverse of temperature for a potassium blue bronze irradiated with 2.5 MeV electrons at a dose of 12 mC/cm². The continuous line shows the cycle with the temperature varying at a constant rate. The arrow shows the relaxation for several hours at about 90 K. Note the weakened temperature dependence of resistance on cooling after the relaxation and, on heating, the anomaly when the relaxation temperature is approached.

Fig. 3. — Resistance in a log scale as a function of temperature for an irradiated potassium blue bronze. The samples of these figures have been room temperature annealed for several days after irradiation. a) This figure shows the hysteresis cycle at constant rate for cooling and heating (solid line) and the influence of the increasing relaxation amplitude on the observed width of the plateau. The memory effect is also amplified by a larger relaxation. b) This figure shows that memory effects are observed both when the relaxation occurs on the heating part of the cycle and when the relaxation is done on cooling.

The amplification of the anomalies after irradiation is a clear evidence of the defect origin of the memory effect. Moreover we have observed that the form of the memory cycle depends on the thermal history after irradiation. The results in figure 2 were obtained for a sample that was irradiated at low temperatures and never heated above 200 K. In figure 3 we present memory cycles for samples that were annealed at room temperature for several days after irradiation. The relaxation now produces well defined plateaus of resistivity that extend over several tens of degrees in temperature. We also observe that the width of the plateaus increases with the relaxation amplitude. It is also worth noting that prolonged relaxation amplifies the memory effect observed on heating. A plateau of resistivity was also observed on cooling after a relaxation that was performed during the heating part of the cycle, (Fig. 3b). In this case the memory effect is also amplified by relaxation.

Results concerning the Hall effect measurements are reported on figure 4. It can be seen in this figure that whatever the experimental procedure (continuous cycling, relaxation, etc.), the resistance and the Hall constant vary in the same way. This implies in the simplest approach that the resistivity is controlled by the number of carriers even though small variations of mobility cannot be excluded. We have to mention that
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Fig. 4. — Hall constant dots and resistance (continuous line) in a log scale as a function of the inverse of temperature. We can note that whatever the temperature variations Hall constant and resistivity vary similarly.

The number of carriers found in our experiment is surprisingly smaller than the published values on non-irradiated samples [18].

A salient feature of the present experimental results is the effect of defects on the observed hysteretic and memory behaviours. Especially the memory effect is seen to develop from a small anomaly to a striking phenomenon when defects are introduced. An important task is now to connect the observed transport property variations with the properties of pinned CDW.

3. Discussion.

As demonstrated by Hall effect measurements, the main source of temperature dependence for low-field electronic transport in CDW phase of the blue bronzes is closely related to a varying number of carriers. In the simplest approach the number of carriers is controlled by single particle excitations across the Peierls gap. An out-of-equilibrium single particle gap, associated with a pinned, out-of-equilibrium $q$ vector, has been indeed proposed as a possible source of hysteretic $R(T)$ behaviour in incommensurate CDW systems [19]. However it is difficult to conciliate a pinned gap value with observations such as a plateau of resistivity and a fixed, temperature independent number of carriers in well relaxed samples.

A very tempting way to explain these behaviours is possible with the model recently proposed to describe the temperature dependence of the $q$-vector in $\text{K}_0.30\text{MoO}_3$ [16]. According to this model, band states situated at an energy $E_0$ above the Fermi level are thermally populated. They control the number of electrons in the doubly degenerate conduction band that suffers the Peierls distortion, with a modulation vector $q$ that is now temperature dependent as following:

$$q/b^* = \frac{\rho_0}{4} \frac{0.5}{\exp((E_0 - E_F)/kT) + 1}. \quad (1)$$

With $E_0 - E_F = 650$ K and the total number of conduction electrons $\rho_0$ slightly less than 3 (which is the ideal stoichiometric value) the measured thermal variation of $q$ is reproduced remarkably well. The authors of the model also conjectured that, at sufficiently low temperatures, the Peierls gap goes beyond 650 K and lowest energy excitations will preferentially populate the separate band states at $E_0$. By going even further we can assume that, at low temperature, conductivity mainly occurs in the band states at $E_0$. Then pinned out-of-equilibrium values of $q$ are necessarily associated with metastable values of carrier concentration, i.e. resistivity. The population of the band at $E_0$ will no longer follow the thermal equilibrium value but lags due to the presence of energy barriers which must be overcome when the pinned $q$ vector is varied. The plateau, like that displayed in figure 3, or the weakened temperature dependence of resistivity (Fig. 2) correspond to a well pinned value of $q$. In these assumptions the memory effects can originate from a $q$-value marked by defects for example.

The idea of low temperature transport occurring in a separate band at $E_0$ is roughly consistent with existing transport data. Our Hall effect measurements give a carrier concentration of the order of $10^{17}$ cm$^{-3}$ around 90 K and, inverting equation (1) and using the known unit cell volume of 1 196 Å$^3$ [20] we find a population of $1.2 \times 10^{18}$ cm$^{-3}$ in the band at $E_0$. Moreover the temperature dependence of resistivity or carrier concentration does not follow any well defined activation law. This is understandable due to the metastability of $q$.

We already mentioned that models based on metastable Peierls gap are not in agreement with our experimental data. Another explanation might be the discommensurate CDW model, in which the thermal variation of $q$ near commensurability is supposed to be due to phase jumps in the CDW between commensurate regions. These ideas have been invoked to explain hysteresis and metastability in TaS$_3$ [21] and in $\text{K}_{0.30}\text{MoO}_3$ [22]. In the latter case a macroscopic polarization of CDW was proposed to explain the observation of inhomogeneous resistance of the sample after passing and releasing a current exceeding the CDW conduction threshold. This effect was associated with charged discommensurations that are compressed to the end of the sample to give an average increase of $q$ in the positive end. In fact an inhomogeneous resistance of the sample, due to a macroscopic polarization of the CDW can also be explained with the present model: the normal carrier concentration at the positive end is lower as a consequence of the increase of $q$ (Eq. (1)) and the resistivity of this half of sample higher, as it was
observed [22]. On the other hand recent nuclear magnetic resonance experiments have not provided unambiguous evidence of discommensurations in CDW [4, 23], so the discommensuration based model is not easily applicable.

Our explanation of the hysteresis and memory effects assumes an action of defects through the pinning of the collective CDW condensate without important changes in the electronic structure. The second assumption is not restrictive: in fact any model in which the carrier concentration is imposed by the value of the q-vector of the Peierls distorted bands can account for the experimental observation. In particular the transport mechanism may be related to electronic states associated with defects or impurities, but experimentally it is difficult to establish whether the electronic transport is intrinsic or extrinsic, in the way it is done for usual semiconductors, where single electron states control the transport properties.

The ideas concerning the metastability of the q-vector are yet to be experimentally verified. X-ray and neutron investigations give convincing evidence in what concerns the q(T) dependence described by equation (1) in non-irradiated samples. However thermal hysteresis in this dependence has never been reported in the time scale (hours) of X-ray or neutron diffraction experiments. Field induced structural changes in the direction of q and the transverse broadening of the CDW satellites have been observed, both in hour and millisecond time scales [24, 25]. Nevertheless, in what concerns the resistivity results, the field seems to induce a relaxation towards equilibrium. It is clear that structural characteristics of the metastable CDW states need experimental verification. Study of irradiated samples might prove useful since their resistivity measurements show considerably amplified deviation from equilibrium. Anyhow a high precision is necessary, a factor of 2 on resistivity, i.e.; carrier concentration, corresponding only to a relative change of the length of q of the order of 10^{-3} at about 90 K.

In the approach we have proposed, the memory effects can be explained according to the simple defect density wave ideas [11]: a value of q can be written according to the positions of mobile atomic lattice defects. Experimentally there is no doubt about the defect origin of the memory effects but the exact mechanisms are beyond the present investigations. However one has to mention that the above observations and results deduced from equation (1) concern an averaged q-vector, but inhomogeneous situations could be encountered due to structural defects in the CDW such as dislocations, stacking faults, etc. Consequently, the pinning of such CDW defects might explain the frozen q-values and the memory effects.

4. Conclusion.

In conclusion, we have observed defect-dependent thermal hysteresis and memory effects in the low-field resistivity of the incommensurate CDW phase of blue bronzes. A consistent picture of these phenomena is obtained assuming modulation wave vector pinning and a conduction process that happens in a band separated from the Peierls distorted bands. The metastable population of this band is directly related to the value of the modulation wave vector through the conservation of the total number of conduction electrons. The defect density wave concept, originally proposed in the case of an incommensurate ferroelectric, is in agreement with our results but at present there is no confirmation of defect migration associated with the memory effects.

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