PHYSICAL REVIEW B VOLUME 34, NUMBER 8 15 OCTOBER 1986

# Disequilibration of the pinned charge-density-wave state by slight changes in temperature

Z. Z. Wang and N. P. Ong
*Department of Physics, Princeton University, Princeton, New Jersey 08544*
(Received 10 July 1986)

By slowly oscillating the temperature $T$ through successively smaller cycles we have constructed a state of the pinned charge-density wave in $TaS_3$ which is found to be free of relaxation for 8 h. We demonstrate the extreme sensitivity of this state to slight changes in $T$. Other properties of the hysteresis in the resistance-versus-temperature plane are described.

In the quasi-one-dimensional charge-density-wave conductors,[1] such as $NbSe_3$, $TaS_3$, $(TaSe_4)_2I$, and $K_{0.3}MoO_3$, the physical properties in the pinned state[2-7] are interesting in their own right. Because of the large number of internal degrees of freedom in the charge-density-wave (CDW) condensate there exist many states in the pinned configuration which are closely similar in energy.[6] When a physical parameter such as the temperature $T$ or strain $S$ is altered slightly the pinned CDW finds itself in a configuration which is remote from true equilibrium. Relaxation towards equilibrium proceeds via a series of violent rearrangements (quakes)[7] in the condensate interspersed with a slow logarithmic creep.[3] The reasons why the pinned CDW is so sensitive to changes in $T$ and $S$ (and why the low-field resistance $R$ should reflect these relaxation processes) are poorly understood at present.

In this paper we present the main results of a systematic study of the thermal hysteresis[2] in the $R$-$T$ plane in $TaS_3$. The trajectory in the $R$-$T$ plane lies higher when the sample is warming than when it is cooling. For reasons discussed below these are called the warming and cooling saturation curves. When the direction of the thermal drift is reversed the system immediately leaves one saturation curve and heads towards the other along a trajectory which we call a transit curve. Nowhere along any of these curves is the system in equilibrium. If $T$ is held constant the system relaxes[3] (via quakes and creep) to the equilibrium line which lies midway between the two saturation curves in the $R$-$T$ plane on a time scale of $10^3$ years. In this paper we are concerned with the opposite sequence of events. Starting with the system as close to equilibrium as feasible we demonstrate that slight changes in temperature $\Delta T$ drive the system away from the equilibrium line towards one of the saturation curves, even when the rate of change $dT/dt$ is as slow as 0.3 mK/s. Utilizing computer control of the substrate temperature we can vary $dT/dt$ from 40 to 0.3 mK/s over the range 90–200 K. $T$ can also be held constant to a stability of $\pm 30$ mK for periods exceeding 20 h. $R$ is measured with a dc current to a precision of 1 in $10^5$ with the field 10 times smaller than threshold.

In a previous attempt[5] to access the equilibrium line a short depinning pulse was used to depin and repin the CDW. In the repinned state $R$ was found to be close to, but not quite on, the equilibrium line. The existence of *two* lines of repinned states (one on each side of the equilibrium line) is evidence that equilibrium is not attained in the repinned state. Here we employ a method analogous to the ac demagnetization of ferromagnets to arrive at the equilibrium state. First, a major hysteresis loop (one which touches both saturation curves) is executed at a rate of 10 mK/s. The target temperature $T_0$ is midway between the two extremal temperatures which differ by 15 K. Thereafter, successively smaller cycles are executed until $T$ zigzags to $T_0$. The system ends up on the equilibrium line, i.e., midway between the saturation curves (Fig. 1). During the next 8 h $T$ is held fixed at $T_0(\pm 30$ mK), while $R$ is closely monitored. As shown in Fig. 2, $R$ is found to be free of relaxation except for occasional small jumps. Following the monitoring period, $T$ is slowly increased to explore the flow away from equilibrium. As shown by the solid line in Fig. 1, $R$ deviates strongly from the equilibrium line to return to the warming saturation

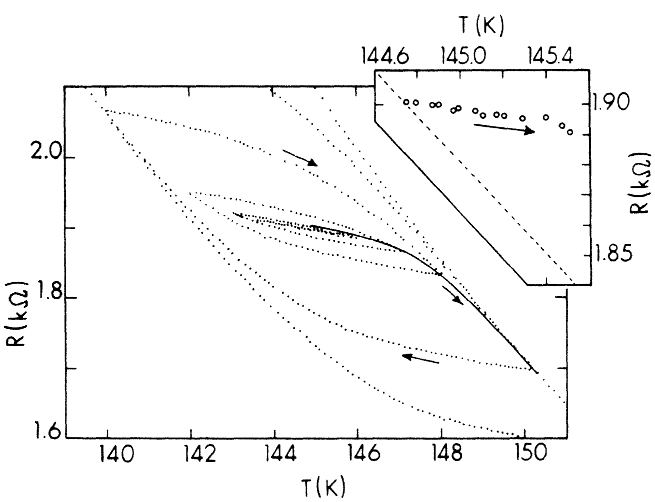


FIG. 1. (Main panel) Construction of the equilibrium state of the pinned charge-density wave in $TaS_3$. The temperature is cycled through successively smaller loops until the equilibrium point at $T_0$ (144.7 K) is reached. The average drift rate is 10 mK/s. The solid line (initial curve) is the trajectory when $T$ is slowly increased (0.3 mK/s) from $T_0$, after a waiting period of 8 h. (Inset) Magnified view of the initial curve near $T_0$. The open circle data are spaced 200 s apart. The equilibrium line (midway between the two saturation curves) is shown by the broken line. Note that $R$ deviates linearly from the equilibrium line.

 

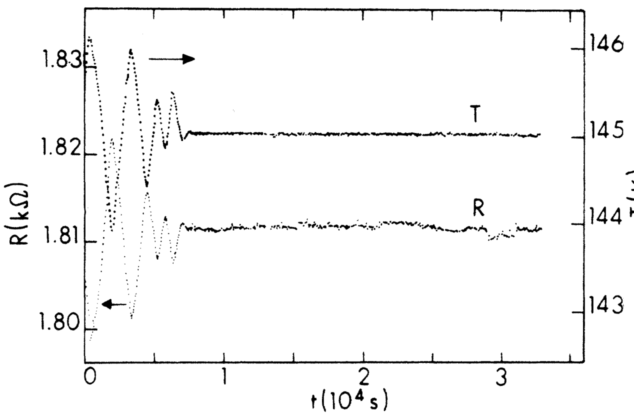


FIG. 2. Stability of the equilibrium state constructed in Fig. 1. The upper (lower) curve shows the variation of temperature (resistance) vs time. The oscillations on the left are the final four minor loops executed before $T$ is stabilized. $R$ is stable to three parts in $10^4$ or 8 h.

curve. Several points are interesting about this curve (called here the initial curve), which is the analog of the remagnetization curve in ferromagnets.

First, the equilibrium condition is very sensitive to slight changes in $T$. In the inset in Fig. 1 we show the departure from equilibrium on an expanded scale (open circle data). Note that deviations from the equilibrium line (shown as a broken line) can be observed for $\Delta T$ as small as 20 mK. Assuming that $\Delta R(T)$ (equals the deviation of $R$ from the equilibrium line) provides some measure of the distance from the equilibrium state at temperature $T$, we infer the disequilibration grows *linearly* with $\Delta T$ even for $\Delta T$ as small as 20 mK: In response to small thermal fluctuations, the system must deviate strongly from equilibrium. Second, the process of disequilibration is independent of the rate $dT/dt$; the same curve is obtained when the initial curve is retraced with the speed reduced from 10 to 0.33 mK/s. (Data for the slower rate are shown as the open circles in the inset of Fig. 1.) The data suggest that the extent to which the system departs from the equilibrium line depends only on $\Delta T$, and is independent of $dT/dt$. Third, the initial curve displays a feature familiar from the study of ferromagnets.[8] When a ferromagnet is demagnetized by slowly oscillating the magnetic field $H$, successively smaller minor loops are executed until $M$ (the magnetization) is zero. Upon remagnetization the $M$ vs $H$ curve passes through the cusps of these minor loops. In Fig. 1 we find to the resolution of our measurements that the initial curve also passes through the warm turning points of the minor hysteresis loops which were previously executed during the approach to equilibrium.

From Fig. 1 it is clear that the initial curve eventually merges with the warming saturation curve as $T$ increases. This behavior (outwards flow) is quite general whenever $dT/dt$ is nonzero. (In Ref. 5 the flow from the repinned state was found to be similar.) We find that regardless of where a state is in the interior of the hysteresis loop, or how it was prepared, the system's trajectory merges with the appropriate saturation curve if $T$ is changed sufficiently ($\Delta T > 5$ K). A path within the loop parallel to, but distinct from the saturation curves is never observed. Neither is a path which intersects either saturation curve. The uniqueness of the saturation curves is quite unexpected in view of the many available metastable configurations mentioned above, and the fact that the system is far from equilibrium on either saturation curve. Thus, a finite $dT/dt$ stabilizes the saturation curves, eventually drawing all states towards it. In this sense it acts like a limit cycle in dynamical systems. In contrast, when $dT/dt$ is zero the flow pattern is inwards, away from the saturation curves towards the equilibrium line. These two observations together suggest that, whereas the system is not in equilibrium on the saturation curves, the relaxation processes are suppressed or overwhelmed by other physical processes which draw the states towards the outer perimeter of the loop.

Mindful of simple relaxation processes one might expect the size of the thermal hysteresis loops to depend on $dT/dt$, since the system is relaxing while the curves are being executed. Instead, we find the surprising result that none of the trajectories on the $R$-$T$ plane depends on either $dT/dt$ or $d^2T/dt^2$. In order to demonstrate this insensitivity we executed a hysteresis loop with a $T$ versus time profile in which $dT/dt$ is varied stepwise over a range of speeds from 0.3 to 10 mK/s. This is compared with a loop executed immediately afterwards at the constant speed 10 mK/s (between the same turning points). From Fig. 3 it is clear that the size and shape of the two loops are identical. Thus the magnitude of $R$ at any given $T$ is only sensitive to the sign of $dT/dt$ (when $dT/dt$ is nonzero). The magnitude of $dT/dt$ or $d^2T/dt^2$ appears to play no role. We have already seen that the initial curve in Fig. 1 is also insensitive to the speed of execution. The same is true of the transit curves which bring the system from one saturation curve to the other when $dT/dt$ changes sign. Quite generally, we conclude that contrary to conclusions drawn from simple arguments the trajectories traced on the $R$-$T$ plane are in some sense dynamically stable and unique.

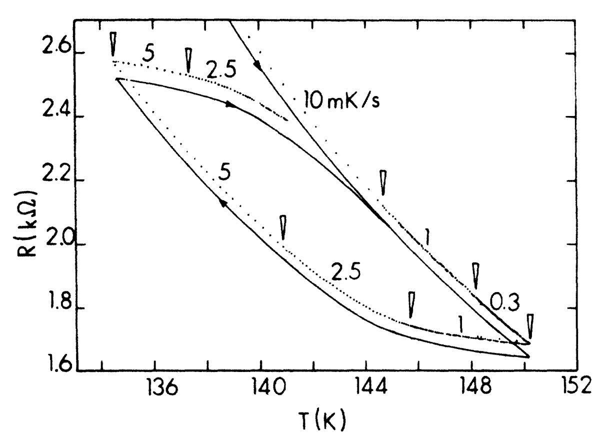


FIG. 3. Comparison of a hysteresis loop executed with stepwise changing speed (data points) with a loop executed at a constant speed of 10 mK/s (solid line). The magnitude of $dT/dt$, indicated in mK/s, is changed abruptly at the places marked by open arrows. For clarity the constant speed loop is displaced downwards by 50 Ω.

The system is drawn to one of the saturation curves whenever $dT/dt$ is nonzero.

The structure of the $R$ vs $T$ hysteresis loops (especially the initial and saturation curves) bears strong similarities to the $M$ vs $H$ and the stress versus strain loops in more familiar physical systems. Many of the features can be phenomenologically explained by Preisach's model.[7,8] However, the differences are also significant. Because the $R$ vs $T$ hysteresis loops can be centered at any $T$ between 50 and 180 K, the relaxation flow pattern in the CDW problem is quite different from, say, the pattern obtained from the "after effect" in ferromagnets. Furthermore, whereas in ferromagnetics[8] reversible behavior is observed whenever domain-wall motion is suppressed (for instance, near saturation), all the paths in the $R$-$T$ plane in the CDW problem are *irreversible;* no path retraces itself when $dT/dt$ changes sign.

What underlies the complicated properties discussed above? Because of the striking reproducibility of the hysteretic loops and the disequilibrating effect that small $\Delta T$ has on the pinned CDW we are persuaded that $\Delta T$ alters one (or several) physical parameter in the system other than the total entropy. A change of the host parameters relative to the condensate parameters exerts a stress on the CDW if the latter cannot readily adjust. The inset in Fig. 1 suggests that once the system locates itself in a deep minimum in the free energy landscape it cannot escape easily when $T$ changes slightly for reasons that are unclear. (In $TaS_3$ the CDW wave vector $Q$ is $T$ dependent above 150 K. This could be the source of the mismatch between the CDW and host. However, it should be noted that in $NbSe_3$ and $K_{0.3}MoO_3$, where much the same hysteretic behavior is observed in the $R$-$T$ plane, $Q$ has been found[9] to be independent of $T$ to 1 part in $10^3$ over the appropriate temperature ranges. Other reasons for a mismatched $Q$ are possible, such as thermal expansion of the host lattice.) In any case, the thermal hysteresis is properly viewed as stress versus strain loops; the CDW is left either in a state of compressive or dilative stress by a slight $\Delta T$. The release of this stress occurs primarily by the spontaneous occurrence of quakes. Consistent with this notion, we find[7] that after each quake the change in $R$ is always *towards* the equilibrium line.

Finally, we discuss the behavior on the transit curves near the turning points (where $dT/dt$ crosses zero). From Fig. 1 we see that $R$ changes very slowly just after each turning point. This is the generally observed behavior in hysteretic systems. ($M$ varies little near a turning point of $H$. The reason is that the "lag" responsible for the hysteresis momentarily narrows when $dH/dt$ crosses zero.) Thus, it is physically sensible from this point of view to treat $R$ as an indicator of the departure from equilibrium of the *total* system (CDW plus quasiparticles). By contrast it would be unreasonable to isolate the CDW response from that of the quasiparticles. For example, it appears plausible that the hysteresis is caused by different magnitudes of the quasiparticle gap $\Delta$ on the two branches. In such a model we would require the derivative $d\Delta/dT$ to jump *discontinuously* at the turning points (because the slope $dR/dT$ is observed to decrease abruptly by almost a factor of 10 after each turning point is crossed). This behavior of $\Delta$ violates the "lag" rule described above. Our results support instead the picture that the quasiparticle density $n_0$ is strongly correlated with the CDW configuration. If the latter is not changing much (as near a turning point) the strong correlation compels $n_0$ to remain roughly constant despite the nominally exponential dependence on $T$. How and why this correlation arises are questions to be further investigated. The rather slow variation of $R$ on the transit curves near the turning point (and on the initial curve near equilibrium) remains one of the most puzzling features of the pinned state.

We acknowledge numerous enlightening discussions with E. Abrahams, P. W. Anderson, S. Coppersmith, and L. Miha'ly.

[1]For a survey, see P. Monceau, in *Electronic Properties of Inorganic Quasi-One-Dimensional Materials,* edited by P. Monceau (Reidel, Dordecht, 1985), Vol. 2, p. 139.

[2]A. W. Higgs and J. C. Gill, Solid State Commun. **47**, 737 (1983); Gy. Hutiray, G. Miha'ly, and L. Miha'ly, Solid State Commun. **47**, 121 (1983).

[3]G. Miha'ly and L. Miha'ly, Phys. Rev. Lett. **52**, 149 (1984).

[4]D. M. Duggan, T. W. Jing, N. P. Ong, and P. A. Lee, Phys. Rev. B **32**, 1397 (1985).

[5]D. M. Duggan and N. P. Ong, Phys. Rev. B **34**, 1375 (1986).

[6]D. S. Fisher, Phys. Rev. B **31**, 1396 (1985); P. B. Littlewood (unpublished).

[7]N. P. Ong and Z. Z. Wang, in *Proceedings of the Conference on Nonlinearity in Condensed Matter, Los Alamos, 1986,* Solid State Sciences (Springer-Verlag, Berlin, in press).

[8]See, for example, *Physics of Magnetism,* edited by Sōshin Chikazumi (Wiley, New York, 1964).

[9]R. M. Fleming, D. E. Moncton, J. D. Axe, and G. S. Brown, Phys. Rev. B **30**, 1877 (1984); R. M. Fleming, L. F. Schneemeyer, and D. E. Moncton, *ibid.* **31**, 899 (1985).