THERMALLY AND ELECTRICALLY INDUCED METASTABLE EPR SPECTRA OF $K_{0.3}Mo_{1-x}V_xO_3$

J. Dumas, B. Laayadi and R. Buder, C.N.R.S. - L.E.P.E.S
BP 166 - 38042 Grenoble Cedex - France.

In pure $K_{0.3}MoO_3$ two separate non-linear CDW conductivity regimes have been observed recently as a function of temperature [1]. While, above ~ 40 K, the CDW dynamics involves viscous damping, a dramatic drop of damping of the sliding motion of the CDW occurs below 40 K ; the CDW condensate moves rigidly above a second abrupt threshold. In order to get insight into the transition between rigid and deformable CDW we have performed EPR studies at 9 GHz (4 K < T < 100 K) of Mo^{5+} centers due to stoichiometry defects.

The EPR spectrum consists of two anisotropic lines with g_A = 1.98, ΔH_A = 17 G, g_B= 1.93, ΔH_B = 15 G when Ho // [102] and the microwave magnetic field h_1 // b-axis. The EPR spectrum arises from a layer near the surface whose thickness can be varied in a reproducible way by etching in ammonia. A relevant thickness of ~ 15 μm is obtained after etching a few hours. Ohmic resistance, threshold fields for depinning with or without switching do not seem to depend noticeably on etching. The EPR spectra, due to the coexistence of commensurate and incommensurate regions [2], depend strongly on the past thermal history of the sample, cooling rate and thermal cycling [3]. The signal amplitude as well as the Ohmic resistance are found to be larger after fast cooling than after slow cooling.

For a given cooling rate, the signal amplitude of line B recorded at a temperature T_m becomes much weaker after subsequent annealing at T_1 = 100 K (Fig.1). However, after annealing at T_1 = 4 K ($T_1 < T_m$), the signal amplitude becomes much larger. In both cases ($T_1 > T_m$), ($T_1 < T_m$) the effect of annealing is pronounced only for $T_m \geq 40$ K.

The EPR line A depends on thermal cyclings in a different manner : after cycling at T_1 = 100 K, a sign reversal of the relative change of the signal amplitude occurs at T_m ~ 32 K (Fig. 2). Flux grown samples of poorer quality show none of these memory effects which reflect the change of the rigidity of the CDW at ~ 40 K[3].

While the Ohmic resistance measured simultaneously in the EPR cavity at a chosen temperature T = 77 K increases with time after quenching ($\Delta R/R$ ~ + 4 % over one hour), the EPR spectra recorded simultaneously remain time in independent ($\Delta I/I$ ~ ± 4 % over one hour). Etching in ammonia leads to reproducible metastable EPR spectra. However, we found non reproducible effects in the time dependence of the Ohmic resistance. There seem to be no clear correlations between threshold fields at 77 K with or without switching and EPR parameters.

(received October 23, 1989)

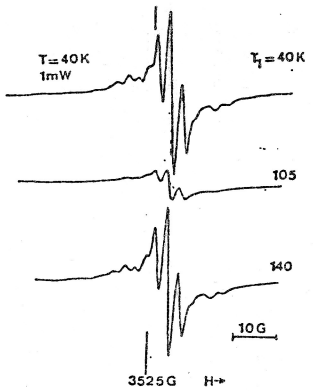

Fig.1a - EPR spectra (line B) recorded at T_m = 40 K after annealing at different temperatures T_1.

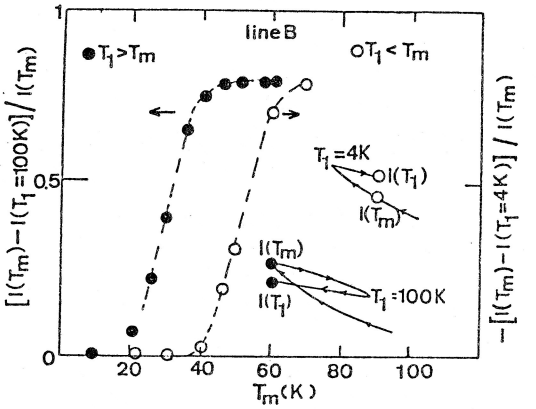

Fig 1b - Left scale (•): Relative change $[I(T_m) - I(T_1 = 100\ K)]/I(T_m)$ in amplitude of the EPR line as a fonction of the temperature T_m at which the spectrum $I(T_m)$ is recorded. Right scale (o): Relative change $-[I(T_m) - I(T_1 = 4\ K)]/I(T_m)$

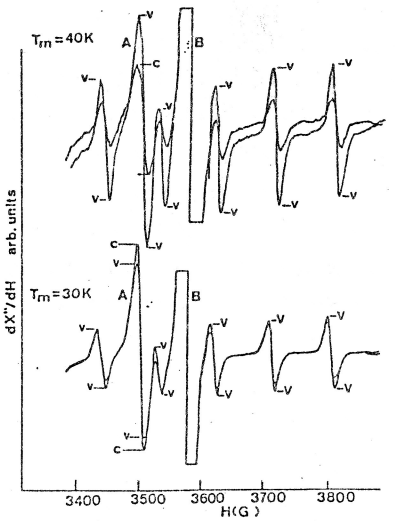

Fig. 2 a. EPR spectra recorded at the two indicated T_m temperatures after annealing at T_1 = 100 K. (v) : virgin state ; (c): cycled at 100 K.

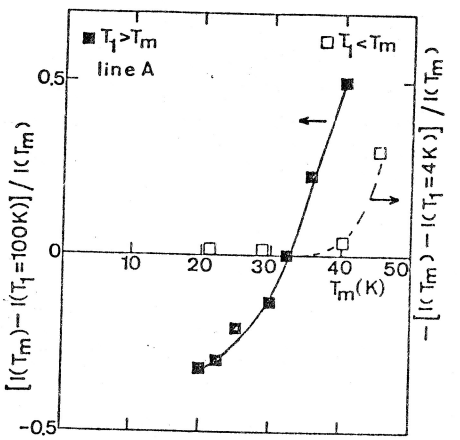

Fig. 2 b. Same as in figure 1b for the line A.

In V-doped samples, the EPR signal arises from both Mo^{5+} ($4d^1$) and V^{4+} ($3d^1$) ions and does not depend on the past history (cooling rate or cycling at 100 K) of the sample. For x ~ 0.02, the V^{4+} hyperfine octet amplitude and the Ohmic resistance do not depend on etching. In pure and V-doped samples, the linewidth ΔH is nearly temperature independent below ~ 40 K and increases rapidly above. The EPR signal vanishes at ~ 100 K. Above ~ 40 K, ΔH obeys the law : log $[\Delta H - \Delta H\ (T = 4\ K)] = E_a\ (x)/k_B T$. The activation energy $E_a(x)$ is comparable to that obtained from resistivity measurements.

In view of these results, we suggest that the Mo^{5+} ions responsible for EPR line B are located near CDW defects on the sites Mo (1) primarily 6+ adjacent to the chains and form therefore weak pinning centers while the non isoelectronic V^{4+}

ions are located on the chains [4] and form strong pinning centers. The additional line (A) could be due to Mo (2) or Mo (3) sites, also near CDW defects, on the conducting chains. The fact that $g_A = 1.98$ and $g_B = 1.93$ seems consistent with a less distorted environment for Mo (2) or Mo (3) sites than for Mo (1) sites. The sign reversal at ~ 32 K in the behavior of the line (A) (Fig. 2) could be due to a redistribution of electrons Mo (1) → Mo (2), and Mo (3).

The metastable behavior in the pinned state at low temperatures can be understood in terms of CDW topological defects, possibly phase dislocations, interacting with lattice defects. It is very likely that the EPR Mo^{5+} ($4d^1$, S = 1/2) active centers act as nucleation and pinning centers for CDW defects. They seem also to appear in thermally induced CDW defects.

The differences of behavior of lines A and B below ~ 30 K reflect some change in the CDW domain configuration. This result should be related to the change in the CDW dynamics below ~ 40 K.

Metastable states can also be electrically induced. At low temperatures (T < 20 K), the EPR spectrum of pure $K_{0.3}MoO_3$ is modified after application an electric field as soon as $E \sim E_t/2$ where E_t is the threshold field. Similar effects are found when the microwave magnetic field h_1 is // or ⊥ the chain axis. After the field is removed, the spectrum relaxes with a time scale of ~ 600 s at 10 K (Fig. 3). These electrically induced deformations of the spectra are similar to that found, on a limited number of samples, for h_1 // or ⊥ to the chain axis, after quenching from 300 K to 10 K [5]. They are very likely related to the strong polarization which can be electrically induced at low temperature (1,6).

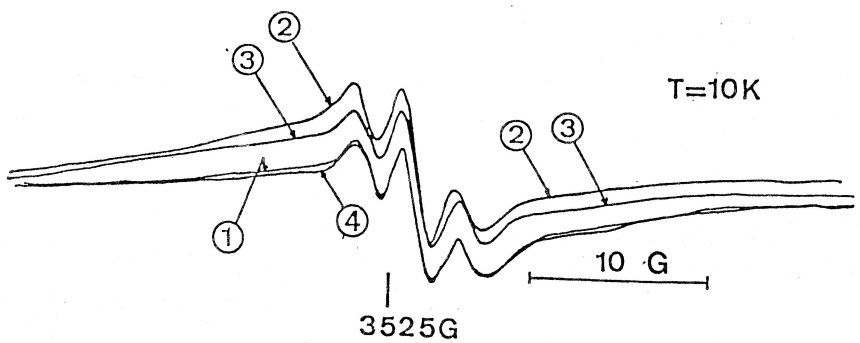

Fig. 3 Metastable deformation of the EPR line B at T = 10 K under an applied voltage (V_t = 7 V) ; 1. virgin state , V = 0 ; 2. V = 6 Volt ; 3. immediately after switching off the voltage ; 4. subsequent spectrum after 15 minutes.

REFERENCES

1 - G. Mihaly, P. Beauchêne, Solid State Comm. 63, 911 (1987).
2 - A. Janossy et al., Phys. Rev. B 38, 1577 (1988).
3 - J. Dumas, B. Laayadi, R. Buder, Phys. Rev. B, 40, 2968 (1988) ; J. Dumas et al. Solid State Comm. to be published.
4 - S. Girault et al., Phys. Rev. B 38, 7980 (1988).
5 - J. Dumas et al., Pysica B 143, 183 (1986).
6 - J. Dumas et al., Synth. Metals 29, F 487 (1989) ; A. Zettl et al., Phys. Rev. B 38, 13002 (1988) ; B. Horovitz, private communication.