

MOSSBAUER STUDY OF THE PEIERLS TRANSITION IN THE QASI-TWO DIMENSIONAL MOLYBDENUM OXIDE γ - Mo_4O_{11}

R. Chevalier, H. Guyot, J. Dumas, R. Buder,
CNRS, LEPES, BP 166, 38042 Grenoble Cedex, France

The quasi-two dimensional molybdenum oxide γ - Mo_4O_{11} shows a Peierls transition at ~ 100 K towards an incommensurate CDW conducting state ^(1,2) associated with partial nesting of the Fermi surface ⁽³⁾. The orthorhombic crystal structure, shown in figure 1, involves Mo O_6 octahedra sharing corners to form infinite slabs, three octahedra thick, which are connected by infinite layers of Mo O_4 tetrahedra. Two consecutive slabs are mirror image of one another. There are four independent Mo sites. The charge distribution is as follows : 6+ for Mo (1) ($4d^0$) tetrahedral sites, 5.8+, 5.4+ and 5+ respectively for the octahedral sites Mo (2), Mo (3) and Mo (4) (Réf. 4).

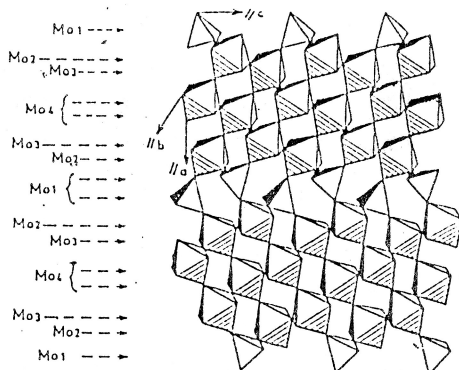


Fig. Idealized crystal structure of γ - Mo_4O_{11} showing Mo O_6 octahedra slabs and Mo O_4 tetrahedra planes.

We report a Mossbauer spectroscopy study of the Peierls transition for single crystals and powders of ^{57}Fe -doped γ - Mo_4O_{11} . The typical concentration of ^{57}Fe in the samples is as low as ~ 100 ppm. Taking into account the local environment of each Mo site, the Mossbauer spectrum, shown in figure 2a, is satisfactorily described by the superposition of four quadrupolar doublets schematically shown in figure 2b. This indicates that ^{57}Fe is substituted both on tetrahedrally and octahedrally coordinated Mo ions. The isomer shift δ of each doublet is found to be proportional to the valence of each corresponding substituted Mo ion, as summarized in figure 3. The largest splitting occurs for the site Mo (1) which has a more distorted environment.

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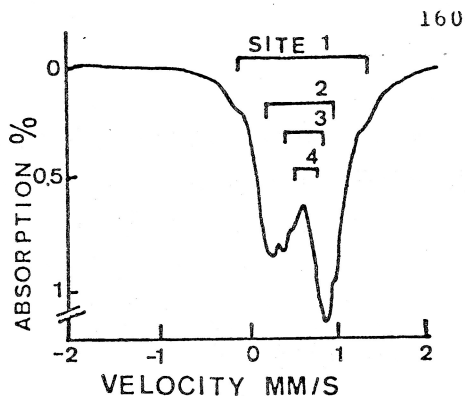


Fig. 2a - Mossbauer spectrum at T = 300K

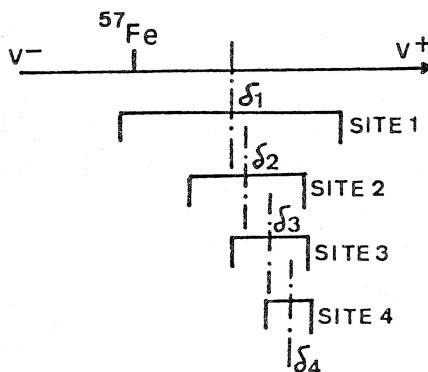


Fig. 2b - Decomposition of the spectrum into four doublets.

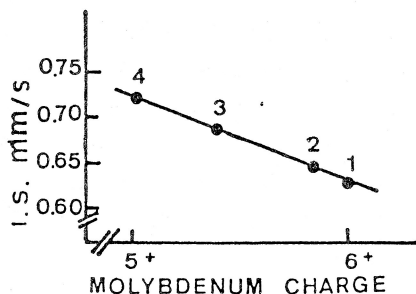


Fig. 3 - Isomer shift δ as a function of the charge on the substituted Mo ion.

Our decomposition of the spectrum is consistent with the fact that an increase in δ implies a decrease of the charge density at the ^{57}Fe nucleus. The most striking feature of our results is that an abrupt decrease in the temperature dependence of the center shift (C.S.) of the spectrum occurs at ~ 100 K. The C.S. is defined as $\sum_i (Y_\infty - Y_i) X_i / \sum_i (Y_\infty - Y_i)$ where Y_∞

represents the background absorption and Y_i the counting rate in the channel X_i . This effect can be ascribed to a decrease at $T_p \sim 100$ K of the intensity of the doublets corresponding to the Mo (3) and Mo (4) sites involved in the onset of the modulated state. This displacement of the C.S. towards negative velocities can be understood in terms of a decrease of the Debye-Waller factor associated to the Mo (3) and Mo (4) sites. From a determination of the Mossbauer intensity, an average decrease of the Mossbauer factor of $\sim 10\%$ at $T = T_p$ is found. This minimum in the C.S. is similar to that found in displacive ferroelectric transitions⁽⁵⁾ (i.e. in PbTiO_3) where a soft phonon mode vanishes at the ferroelectric transition.

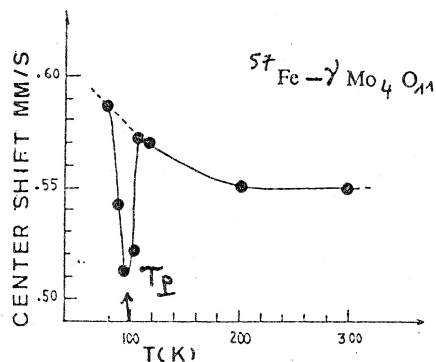


Fig. 4 - Center shift of the spectrum as a function of temperature.

In our case, the anomaly at ~ 100 K indicates that the Mo (3) and Mo (4) sites are predominantly affected by the CDW. The behavior of the C.S. in the temperature interval $100 \text{ K} < T < 200 \text{ K}$ may be due either to a contribution of the second order Doppler shift or more likely to precursor effects.

Mossbauer studies on the related material ^{57}Fe -doped $\text{K}_{0.3}\text{MoO}_3$ show no anomaly in the C.S. at the metal-insulator Peierls transition $T_p = 180 \text{ K}$. In this quasi one dimensional blue bronze ^{57}Fe is also substituted on the Mo sites. The electric field gradient axis at the Mo (2) and Mo (3) sites are rotating at the Peierls transition temperature. In addition, a decrease of the normalized intensity of the spectrum (defined as in Ref. 5) is observed (7). These results may be explained at least qualitatively if one assumes that the three independent Mo sites are equally affected by the Peierls transition below which the Mo atoms, mainly Mo (2) and Mo (3) sites, involved in the chains of the crystal structure show a transverse displacement (8).

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