

# VALENCE DENSITY WAVES IN ONE DIMENSIONAL VALENCE FLUCTUATING SYSTEMS.

M. Avignon

Laboratoire d'Etudes des Propriétés Electroniques des Solides

C.N.R.S. - BP 166 - 38042 Grenoble Cedex, France

Associated with University Joseph Fourier - Grenoble

H. Zheng

Department of Applied Physics, Shanghai Jiao Tong University, Shanghai, P.R. China.

The effects of electron-lattice interaction are very strong in most rare-earth fluctuating valence compounds. The valence changes resulting from electronic transitions from the localized f-shell ( $f^{(n)}$  configuration) to the much wider d band [ $f^{(n-1)}d$ ] are accompanied by important changes in the ionic radii of the rare-earth ions (1). This is supported by many experimental observations such as an anomalously large compressibility in the valence transition region (2), phonon softening (3,4) and large phonon linewidth (4).

We consider a one-dimensional model with alternating rare-earth ions (M) and chalcogens (X) to mimic systems like SmS (Fig. 1). A similar class of materials consisting of transition metal ions linked by halogens is also of great interest (5) and has been considered recently within a different model (6). We start from the simplest spinless tight-binding model to describe the valence fluctuating ions (M), accounting for charge degrees of freedom only :

$$H_0 = \sum_i \epsilon_{di} d_i^\dagger d_i - t \sum_i (d_{i+1}^\dagger d_i + hc) + \sum_i \epsilon_{fi} f_i^\dagger f_i + \sum_i V_i (d_i^\dagger f_i + f_i^\dagger d_i) \quad (1)$$

where the f states are localized while d states are itinerant with nearest neighbour hopping  $t$ . The last term represents hybridization between f and d states which is taken as local. We will consider only the symmetric case in the absence of electron lattice interaction ( $\epsilon_{di} = \epsilon_d$ ,  $\epsilon_{fi} = \epsilon_f$  and  $\epsilon_d = \epsilon_f$ ) with one electron per metallic ion M ( $n_d + n_f = 1$ ), leading to  $n_d = n_f = \frac{1}{2}$  for any value of  $V$  with the Fermi level  $\epsilon_F$  at  $\epsilon_d = \epsilon_f$ . (We can take  $\epsilon_d = \epsilon_f = 0$ .)

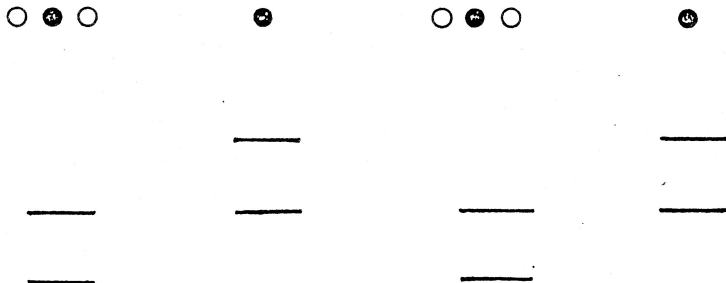


Fig. 1

(received December 27, 1989)

In general  $\epsilon_{di}$ ,  $\epsilon_{fi}$  and  $V_i$  can all depend on the position of the surrounding chalcogen ions, however in this paper we consider only the d electron-lattice coupling, keeping :  $\epsilon_{fi} = \epsilon_f$  and  $V_i = V$

$$\epsilon_{di} = -\lambda q_i. \quad (2)$$

$q_i$  being the coordinate of the local mode.

Then, including the elastic part, the electron-lattice part  $H_1$  of the Hamiltonian can be written as

$$H_1 = -\lambda \sum_i q_i d_i^+ d_i + \sum_i \frac{K}{2} q_i^2 \quad (3)$$

In the absence of hybridization the conduction band is half-filled, so one expects to have Peierls instability with respect to alternating lattice distortion

$$q_i = (-)^i m_p \quad (4)$$

producing the classical gap for  $k = \frac{\pi}{2a}$  around the Fermi energy ( $\epsilon_F = \epsilon_f = 0$ ) and giving rise to d-charge ordering.

Non-zero hybridization also produces a gap around  $\epsilon_f = 0$  even in the absence of electron lattice coupling ( $\lambda = 0$ ), so one may ask whether the system still remains unstable with respect to the lattice distortion (4). The total Hamiltonian can be diagonalized in the k-space. For  $V = 0$ , one simply gets the two bands

$$\epsilon_{\pm}(k) = \pm \sqrt{\epsilon_k^2 + \lambda^2 m_p^2} \quad (5)$$

with  $\epsilon_k = 2 t \cos ka$

while for  $V \neq 0$ , four bands are obtained

$$E(k) = \frac{1}{2} \left( \epsilon_{\pm}(k) \mp \sqrt{\epsilon_{\pm}^2(k) + 4 V^2} \right) \quad (6)$$

resulting from the hybridization of bands  $\epsilon_{-}(k)$  and  $\epsilon_{+}(k)$  with the f level. The lowest two are occupied,  $\epsilon_F$  remains at zero and one still has  $n_d = n_f = \frac{1}{2}$ .

The ground state energy is obtained in the following form :

$$E_g = -\frac{2t}{\pi} \left( 1 + \overline{\lambda^2 m_p^2 + 4 \overline{V^2}} \right)^{1/2} E(\pi/2, q) + \frac{K}{2} m_p^2 \quad (7)$$

$E(\pi/2, q)$  being the complete elliptic integral of the second kind of parameter

$$q = (1 + \overline{\lambda^2 m_p^2 + 4 \overline{V^2}})^{-1/2}, \quad q < 1 \quad (8)$$

with  $\overline{\lambda} = \lambda/2 t$  and  $\overline{V} = V/2t$ .

The dimerization parameter  $m_p$  is determined by the minimum of  $E_g$ , i.e. :

$$K m_p = \frac{\lambda^2 m_p}{\pi} q F(\pi/2, q) \quad (9)$$

$F(\pi/2, q)$  is the complete elliptic integral of the first kind.

The d and f electron ordering parameters are defined respectively as

$$m_d = \frac{1}{N} \sum_i (-)^i \langle d_i^+ d_i \rangle$$

$$m_f = \frac{1}{N} \sum_i (-)^i \langle f_i^+ f_i \rangle \quad (10)$$

They are obtained from  $d$  and  $f$  Green's function and

$$m_d = -m_f = -\frac{K}{\lambda} m_p \quad (11)$$

Beside the solution  $m_p = 0$ , eq. (9) always has a solution for  $q$ ,  $q = q_e$ . Then from (8) one immediately sees that the solution  $m_p$  decreases for increasing  $\bar{V}$  until  $\bar{V}$  reaches the critical value  $\bar{V}_c$  such that  $\frac{1}{\sqrt{1 + 4\bar{V}^2}} = q_e$  for which  $m_p = 0$ . Since  $q_e$  increases for

decreasing  $J = \lambda^2/K$ ,  $\bar{V}_c$  increases when  $J$  increases.

For  $\bar{V} > \bar{V}_c$ , only the solution  $m_p = 0$  exists and the system cannot dimerize (UD), while for  $\bar{V} < \bar{V}_c$  the dimerization exists (D) leading to  $d$ - and  $f$ -charge ordering (valence density wave) (Fig. 2). Similar dynamic valence density wave has been envisaged in SmS resulting from the coupling with longitudinal phonons (7).

The resulting phase diagram in the  $(J, \bar{V})$  plane is shown in Fig. 3. However, relation (11) immediately shows that the total charge  $n_{di} + n_{fi}$  remains the same on each site, so that the system do not present charge ordering.

It would be of interest to consider also the coupling of  $f$ -electrons with the lattice which has often been used to describe electron-phonon interaction in fluctuating valence systems (8,9). This will be presented elsewhere.

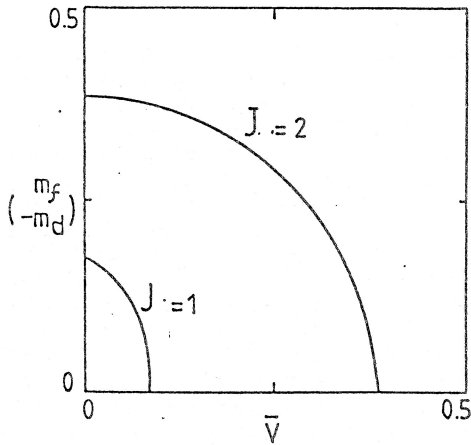


Fig. 2

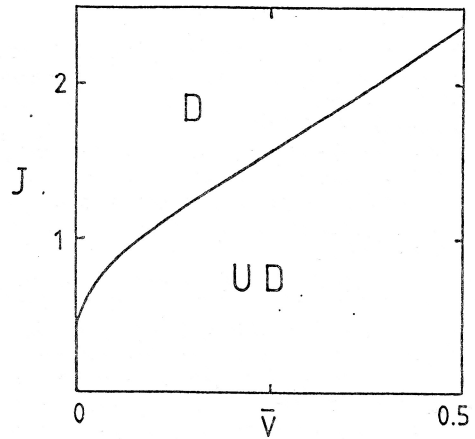


Fig. 3

## REFERENCES

- 1 - For a review on valence fluctuation phenomena see for example : J.M. Lawrence, P.S. Riseborough and R.D. Parks, Reports on Progress in Physics, 44, 1 (1981).
- 2 - A. Jayaraman et al, Phys. Rev. B 9, 2513 (1974).
- 3 - G. Güntherodt et al, Solid State Comm. 27, 551 (1978).
- 4 - H.A. Mook et al, Phys. Rev. B 18, 2925 (1978).
- 5 - See for instance, H.J. Keller, Extended Linear Chain Compounds, Vol. 1, ed. J.S. Miller (New York : Plenum Press) p. 357.
- 6 - S. Ichinose, Solid State Comm. 50, 137 (1984).  
D. Baeriswyl and A.R. Bishop, J. Phys. C 21, 339 (1988).
- 7 - K.H. Bennemann and M. Avignon, Solid State Comm. 31, 645 (1979).
- 8 - D. Sherrington and S. Von Molnar, Solid State Comm. 16, 1347 (1975).
- 9 - S. Ichinose and Y. Kuroda, Phys. Rev. B. 25, 2550 (1982) and references therein.