VALENCE DENSITY WAVES IN ONE DIMENSIONAL VALENCE FLUCTUATING SYSTEMS.

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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 :

$$H_0 = \sum_i \varepsilon_{di}\, d_i^+ d_i - t \sum_i (d_{i+1}^+ d_i + hc) + \sum_i \varepsilon_{fi}\, f_i^+ f_i + \sum_i V_i\, (d_i^+ f_i + f_i^+ d_i) \qquad (1)$$

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 ($\varepsilon_{di} = \varepsilon_d$, $\varepsilon_{fi} = \varepsilon_f$ and $\varepsilon_d = \varepsilon_f$)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 ε_F at $\varepsilon_d = \varepsilon_f$. (We can take $\varepsilon_d = \varepsilon_f = 0$.)

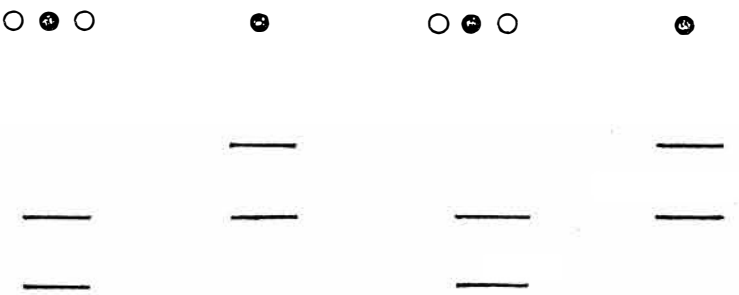

Fig. 1

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In general ε_{di}, ε_{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 : $\varepsilon_{fi} = \varepsilon_f$ and $V_i = V$

$$\varepsilon_{di} = -\lambda q_i. \tag{2}$$

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

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

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

$$q_i = (-)^i m_p \tag{4}$$

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

Non-zero hybridization also produces a gap around $\varepsilon_f = 0$ 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

$$\varepsilon_\pm (k) = \pm \sqrt{\varepsilon^2_k + \lambda^2 m_p^2} \tag{5}$$

with $\varepsilon_k = 2\,t \cos ka$

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

$$E_{(k)} = \frac{1}{2}\left(\varepsilon_\pm(k) \mp \sqrt{\varepsilon^2_\pm(k) + 4\,V^2}\right) \tag{6}$$

resulting from the hybridization of bands $\varepsilon_-(k)$ and $\varepsilon_+(k)$ with the f level. The lowest two are occupied, ε_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 :

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

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

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

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

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

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

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

The d and f electron ordering parameters are defined respectively as

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

$$m_f = \frac{1}{N}\sum_i (-)^i < f_i^+ f_i > \tag{10}$$

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

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

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 $\overline{V}$ until $\overline{V}$ reaches the critical value $\overline{V}_c$ such that $\frac{1}{\sqrt{1 + 4\overline{V}^2}} = q_e$ for which $m_p = 0$. Since q_e increases for decreasing $J = \lambda^2/K$, $\overline{V}_c$ increases when J increases.

For $\overline{V} > \overline{V}_c$, only the solution $m_p = 0$ exists and the system cannot dimerize (UD), while for $\overline{V} < \overline{V}_c$ 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 $(J, \overline{V})$ 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.

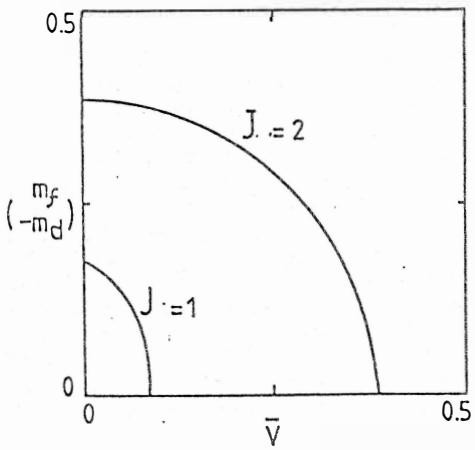

Fig. 2

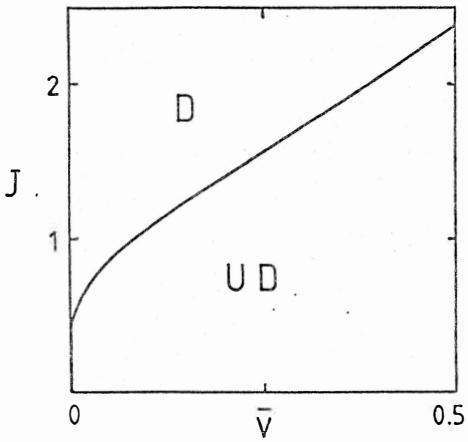

Fig. 3

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