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Theory for the mixed-valence state

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Résumé. — Une théorie est présentée qui explique pourquoi les composés de type valence-mixte se comportent comme un liquide de Fermi à deux composantes ; la théorie explique aussi le fait que TmSe possède un ordre magnétique, alors que les autres composés n’en possèdent pas. La variation de $T_N$ et du champ $H_T$ pour l’alignement ferromagnétique, en fonction du rapport $\text{Tm}^{2+}/\text{Tm}^{3+}$, est expliquée de façon quantitative. Nous pouvons prédire que TmSe s’ordonne ferromagnétiquement pour une concentration de $\text{Tm}^{2+} \gtrsim 0.3$.

Abstract. — A theory is presented which explains why mixed-valence compounds behave as two component Fermi liquids, and why TmSe orders magnetically while the other known mixed-valence compounds do not. The variation of $T_N$ and the field $H_T$ to obtain ferromagnetic alignment with changing $\text{Tm}^{2+}/\text{Tm}^{3+}$ ratio is quantitatively explained. For $\text{Tm}^{2+}$ concentration $\gtrsim 0.3$, TmSe is predicted to order ferromagnetically.

The experimental results on homogeneous, mixed-valence compounds and alloys (HMV) suggest their characterization as two component Fermi liquids, one with a degeneracy temperature of a few eV and the other, undoubtedly associated with f-electrons, with a degeneracy temperature of 0.01-0.1 eV. Among the known HMV materials, TmSe is unique in that it exhibits magnetic order at low temperatures.

A theory has been constructed to understand the above mentioned behaviour. I present here an extended abstract of the work. First a Hamiltonian is constructed which gives rise to mixed-valence behaviour at an isolated site. This means that two different f-configurations at the site are nearly degenerate and Friedel’s rule is observed for each one of them. Such a situation can be brought about only through consideration of local lattice deformations and/or by electronic screening. One of the conclusions is that any configuration differs from integral occupation only by $0(\Delta/U)$, where $\Delta$ is the effective f-level width and $U$ is the intrasite electron-electron repulsion energy. Next, interaction between two mixed-valence impurities brought about by the hybridization of the f-levels with the d-bands is calculated. We consider the interactions in the following cases:

(a) Site i and site j occupied by the same charge and spin configuration.

(b) Site i and site j occupied by the same charge but different spin configurations.

(c) Site i and site j occupied by different charge configurations.

The interaction energy in cases (a) and (b) is of $0(\Delta^2/U)$. In case (c) the interaction energy is (much larger than cases (a) and (b)) of $0(\Delta)$; but the important point is that this energy is indifferent to the spin configuration at one site if the other site has a configuration with net spin zero. If both sites have finite net spins, the interaction in (c) favors a mutual ferromagnetic alignment at sites i and j. Case (c) represents the classic double exchange interaction.

Now one or the other valence configuration of all known HMV materials except TmSe is nonmagnetic. For such materials, case (c) merely represents a kinetic energy lowering of $0(\Delta)$ without any prejudicial magnetic interactions, while cases (a) and (b) represent the magnetic interactions. A simple Stoner criteria can now be invoked to show that these materials will not exhibit any magnetic ordering and that simple Fermi liquid behaviour follows.

TmSe is a different case. TmSe is observed to order antiferromagnetically at $T_s = 3.2$ K, and $T_s$ and $H_T$, the field to obtain ferromagnetic alignment for $T \to 0$, depend strongly on the valence ratio $\text{Tm}^{2+}/\text{Tm}^{3+}$. The observed properties of TmSe can be quantitatively explained by using the fact that case (c) leads to ferromagnetic interactions in TmSe, and that the strength of the interactions increases as the valence ratio increases. A prediction following from this work is that with $\text{Tm}^{2+}$ concentration in excess of $\approx 0.30$, TmSe will order ferromagnetically.