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ABNORMAL ORDERED KONDO LATTICE

A. BENOIT, J. FLOUQUET, M. RIBAUT

Laboratoire de Physique des Solides, Université Paris-Sud
 Bât. 510, 91405 Orsay Cedex France

F. FLOUQUET

Laboratoire de Photophysique moléculaire, Université Paris-Sud,
 91405 Orsay Cedex France

G. CHOUTEAU and R. TOURNIER

Laboratoire des Très Basses Températures C.N.R.S. 38000 Grenoble France

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Résumé. — En utilisant un modèle simple, nous calculons à 0 K l'état fondamental des composés intermétalliques de cérium et obtenons la valeur du coefficient de chaleur spécifique linéaire en température. Dans le régime des composés ordonnés magnétiquement apparaît un cas anormal qui semble avoir la même propriété que le comportement Kondo trouvé dans les alliages dilués.

Abstract. — Using a very crude model, we calculate at 0 K the magnetic ground state of the cerium intermetallic compounds and derive the corresponding value of the linear temperature coefficient of the specific heat. In the ordered systems, an abnormal point appears due to the variation of the symmetry. This point seems to reflect the same property as the Kondo point of the local magnetism problem.

1. Introduction. — All the abnormal intermetallic compounds of cerium like Al_3Ce , Al_2Ce , In_3Ce , Sn_3Ce are characterized by a high linear temperature dependence coefficient γ of their specific heats $C = \gamma T$ [1].

These high values of γ indicate the occurrence of a high density of states at the Fermi level, that is to say low energy excitations as is found for an isolated Kondo impurity for amorphous materials or for spin glasses. At high temperature the Ce ion is defined by its local exchange coupling with the Fermi sea. At low temperature, we must take into account the importance of local excitations (Kondo coupling) with respect to exchange coupling produced by the other ions (possibility of collective excitations).

In a first step, the magnetic ground state is determined at 0 K; in a second step, the γ coefficients are derived using a simple relation for the disappearance of the Kondo anomaly by the magnetic ordering.

The expressions which have been chosen to describe the Kondo correlation of each ion with the Fermi sea are not crucial. Quantitatively the exact shape of the results such as the γ coefficient depends on the initial

expressions, but the anomalies which will be found are of the same nature. We emphasize that the exact physical situation of these abnormal rare earth compounds corresponds to the cases where the Kondo coupling has the same magnitude as the exchange couplings. When these last terms are much larger than the Kondo coupling, the trivial situation of the normal intermetallic compound must be found. We have not tried to obtain an exact extrapolation for a vanishing Kondo coupling.

2. Basis of the model. — Single ion parameter. The behaviour of an isolated Kondo impurity is now well established at low temperature. At 0 K, the ground state is a singlet which remains polarizable by an applied field. A simple law for the polarization can be given by :

$$M \sim \frac{2}{\pi} \text{Arc tg } \frac{\mu_B H}{k_B T_K} \quad (1)$$

The low temperature properties can be derived in the same spirit as in the usual Landau theory of Fermi

liquids [2]. For example, the linear temperature dependence coefficient γ of the specific heat can be approximated by the relation [3]

$$\gamma = \frac{kT_K}{(kT_K)^2 + (\mu_B H)^2} \quad (2)$$

This Kondo description must be corrected for crystal field effects. Usually in a cubic symmetry, the ground state is the doublet Γ_7 which is completely isotropic and reducible to a spin one half with a magnetic moment of $0.81 \mu_B$.

The polarization of the doublet by the applied field leads to a crystalline anisotropy. (See reference [4] for example.) In order to take into account this Van Vleck polarization, we have chosen the following magnetization law with a single anisotropy angle parameter θ

$$M = M_0 \left[\frac{2}{\pi} \text{Arc tg} \frac{\mu_B H}{k_B T_K} + G(\theta) H \right] = M_0 F(H, \theta) \quad (3)$$

The energy of the well-isolated Kondo ion is given by a function $E_K(x, \theta)$ where $x = M/M_0$. In zero field, the minima value $E_K = 0$ corresponds to $M = 0$. In an applied field H , E_K must give the magnetization law. By minimizing the total energy, we arrive at the differential equation :

$$\frac{\partial E_K}{\partial x} = M_0 H.$$

The expression (3) defines the relation $F^*(x, \theta)$ between the applied field and the two parameters x and θ :

$$H = F^*(x, \theta).$$

The function $E_K(x, \theta)$ is then equal to :

$$E_K(x, \theta) = M_0 \int_0^x F^*(x, \theta) dx.$$

In dilute alloys the correlation parameter T_K is linked to the local exchange parameter J and the density of states ρ at the Fermi sea by the relation :

$$T_K = T_F \exp - \frac{1}{2J\rho} \quad T_F \sim 1/\rho.$$

In the abnormal compounds, T_K is only a phenomenological parameter related in fact to the Jullien *et al.* theory of the Kondo lattice [16].

3. Interaction parameters. — In the dilute limit or for ordinary metals of the rare earth series, the interaction between the ions is simply described by the exchange hamiltonian

$$E = J_{12} \mathbf{M}_1 \cdot \mathbf{M}_2 \quad \text{with} \quad J_{12} \sim J^2 \rho \quad (4)$$

where J_{12} represents the indirect coupling between the ions *via* the Rudermann Kittel polarization of the Fermi sea ; it must be emphasized that in dilute alloys the form of the interaction is correct even in the presence of the Kondo effect as has been shown theoretically [5] and experimentally [6, 7]. In the case of strongly correlated electron gas, the relationship between T_K and the coupling constant J_{12} must be modified since the exchange coupling and the bandwidth of the conduction electrons cannot be regarded as independant parameters. We will assume an exchange coupling between the magnetic moments restricted to first neighbour ferromagnetic and second neighbour antiferromagnetic interactions. Each ion is magnetized using the singlet law [1] under the action of the fictitious field $\mathbf{H}_i = \sum J_{ij} \mathbf{M}_j$.

An excellent example is given by the Al_2Ce compound. At low temperature, the occurrence of cooperative phenomena between the cerium ions is clearly shown in the correlation parameter T_K and the long range order observed below a critical temperature T_M ($T_K \sim 6 \text{ K}$, $T_M \sim 3.8 \text{ K}$ see ref. [18]). At high temperature, the ions can be regarded as independent of each other ; they are characterized by a Kondo coupling T'_K which is an order of magnitude lower than T_K ($T'_K \leq 0.1 \text{ K}$ from ref. [19] and [20]).

4. Calculation. — We shall now solve the problem of the stable configuration of a linear chain of ions at 0 K and try to derive the value of the corresponding γ coefficient. All stable solutions despite the trivial solution $M = 0$ will be an ordered periodic structure. Inside the chain, the spins are assumed to be in parallel planes ; this includes the complet basis of sinusoidal or helicoidal modes. The magnetization of each ion will be characterized by its modulus $x_i = M_i/M_0$ and the angle θ_i made with a given direction in the planes. N being the number of spins in a period, the solutions of minimal energy are sought for different values of N (0 to 10), the chosen period corresponds to the lowest minimum. The anisotropy term has the following form

$$G(\theta) = K_0(2 + \cos 4\theta)$$

in the calculation. Taking into account the single ion properties and the inter-ion exchange coupling, the expression of the total energy per ion is then :

$$E_{\text{total}}(x_i, \theta_i) = \frac{1}{N} \left[\sum_{i=1}^N E(x_i) + \sum_{i=1}^N M_0^2 J_1 x_i x_{i+1} \cos(\theta_i - \theta_{i+1}) + \sum_{i=1}^N M_0^2 J_2 x_i x_{i+2} \cos(\theta_i - \theta_{i+2}) \right].$$

The minima of this expression are computed by a subroutine which gives only the partial minima for given initial conditions. The calculation is made by

iteration using random values of θ_i . Generally the choice of the minimum is unambiguous. It must be underlined that when the stable ordered structure changes its symmetry (transition from planar to axial), the corresponding minima are very close. Different initial conditions must be chosen in order to find the real minimum.

When the Kondo temperature increases for constant values of the exchange parameters (J_1 , J_2) (Fig. 1), the following ground states are found :

— For $T_K < T_{K_1}$ a helicoidal magnetic structure with planar symmetry :

$$M_x = M \cos \mathbf{qr} \quad M_y = M \sin \mathbf{qr}$$

with $M_i \neq M_0$.

— For $T_{K_1} < T_K < T_{K_2}$ a modulated structure of axial symmetry z :

$$M_z = M \cos \mathbf{qr} \quad \text{with} \quad M_i \neq M_0$$

and

$$M_i \rightarrow 0 \quad \text{when} \quad T_K \rightarrow T_{K_2}.$$

— For $T_K > T_{K_2}$ a non-magnetic Kondo ground state.

At T_{K_2} a second-order transition occurs, at T_{K_1} a first order. Using a simple expression for the correlation energy :

$$E_K = \text{const.} (k_B T_K - \alpha \cos 4\theta) M^2 + \beta M^4$$

it can be shown that $T_{K_2} - T_{K_1} = 5.5 \alpha$.

The values of γ reported on figure 1 are obtained by averaging expression (2) over a period; the two singular points T_{K_1} and T_{K_2} appear clearly.

For a modulated structure and a supplementary coupling interchain of $J_3 = 17$ kOe, it must be emphasized that the theoretical magnetization reproduces

FIG. 1. — In arbitrary units, the value of γ (the linear temperature dependence of the specific heat) as a function of the reduced correlation parameter $k_B T_K / J_1$. The parameters are taken as

$$J_1 = -100 \text{ kOe}, \quad J_2 = +40 \text{ kOe}, \quad K_0 = 7 \times 10^{-4} \text{ kOe}^{-1}.$$

P and A indicates the symmetry of the helicoidal and sinusoidal modes.

exactly the results of the experiments [4], [8] performed on the Al_2Ce compound known recently as a modulated structure [9].

5. Discussion. — The first anomaly at T_{K_2} will be called the Kondo lattice instability and is simply the transition from a non-ordered to an ordered structure. The true maximum of γ may be steeper than the value found here. The T_{K_2} anomaly can be understood by comparison with the appearance of the magnetism of an atom pair in dilute alloys. Let us regard the Kondo variation of a single ion characterized by its T_{K_0} coupled with another ion by a ferromagnetic molecular field M . The T_K of the pairs is now :

$$T_K = T_{K_0} \left[1 - \frac{\lambda}{\lambda_c} \right]$$

where λ_c is the occurrence of a free paramagnetic pair object (the magnetic instability). Since γ varies as $1/T_K$ in the non-magnetic region, a divergence occurs at the magnetic instability [6].

The second anomaly at T_{K_1} is more interesting. The problem of the crossing of two levels in interaction with a continuum may have spectacular properties. A general discussion is given in the review of Wilson on the renormalization group [17]. For an experimentalist, many cases may be found.

An excellent example is even given in molecular physics for the photo dissociation of the H_2O molecule in its second excited state [13]. When the molecule is linear, the excited and ground states have different symmetry and can have level crossing (conical intersection). On the other hand, for the bend geometry the two states of the same symmetry cannot cross over. The conical intersection leads to curious topological potential energy surfaces and consequently to the abnormal high rotation energy of an $\text{OH} (^2\Sigma^+)$ fragment by interaction with the quasicontinuum which comes from the ground state.

Here the minimization of the energy shows that different collective modes may occur at T_{K_1} and their respective symmetry will be the crucial problem. Due to the strong interaction with the Fermi sea, a high density of collective modes occurs at T_{K_1} which leads to an unusual high value of γ .

Our model of well-localized itinerant fermions has been derived by analogy with the Blandin Friedel approach to the appearance of local magnetism in normal metals [11]. The simple argument is that the local magnetism occurrence is theoretically an N -body problem but that a H.F. picture is a good approximation so that it is correct for a description with only one degree of freedom of the magnetic moment.

The H.F. parameter γ can be simply derived from the value of the density of states of the virtual level at the Fermi energy; a maximum of γ occurs just

at the magnetic instability in a symmetrical model. When all the degrees of freedom of the magnetic moment are taken into account, its degeneracy leads to the Kondo problem by interaction with the continuum. At the unstable ordered point T_{K_1} , the initial degeneracy of the ground state (helical and sinusoidal mode) in strong interaction with the Fermi sea can be regarded as the physical situation found in the local Kondo problem [10]. It can be predicted that for the instability point T_{K_1} , the collective mode may have the property of a Kondo impurity.

The striking point is that the abnormal cerium compounds seem to be well described by our phenomenological model. All the compounds known now as well-ordered (Al_2Ce , In_3Ce [1]) have an almost constant value of $\gamma \sim 200 \text{ mJ/K}^2/\text{mole}$; the importance of the magnetic anisotropy is reflected in the remanent properties. The Al_3Ce compound which has an abnormally high value of

$$\gamma \sim 2000 \text{ mJ/K}^2/\text{mole}$$

seems to fulfil exactly the behaviour of the border point T_{K_1} ($T_K = T_{K_1} - \varepsilon$). By decreasing the temperature two specific heat maxima are observed in a small range of temperatures and the change in symmetry is strongly reflected in the remanent property, the magnetization of the sample is almost linear with the field up to 70 kOe and temperature-independent below 4 K [12]. The value of the ratio of the susceptibility to γ and the T^2 law of the resistivity are other proofs of the Kondo-like behaviour [12, 14]. Furthermore by increasing the pressure and then T_K , the γ specific heat coefficient decreases, the specific heat has only one peak and the remanent is constant below the ordering temperature [15]. Finally, the instability of T_{K_1} is reflected in the hysteresis shown by the samples after temperature or pressure cycles [15]. It must be pointed out that recently Bredl *et al.* [18] have interpreted the magnetic properties of the $\text{Al}_2\text{La}_x\text{Ce}_{1-x}$ alloys using a simple resonance level model similar to our approach; the detail of the

magnetic order is not discussed but only the thermal variation of the electronic properties. Similarly, a phase diagram in temperature can be derived here; only one transition occurs for $T_{K_1} < T_K < T_{K_2}$ and two for $T_K < T_{K_1}$.

6. Conclusion. — Our model is the first attempt to describe the possible long-range order of the Kondo lattice. The estimation of γ even with the crude phenomenological expression (2) is in excellent agreement with the experiments. Further theoretical developments must elucidate our phenomenological approach. Our chain of strongly-interacting Kondo ions is a simple example of well-localized fermions. Near the melting point and the magnetic transition, the ^3He fermions of the solid may have some properties found in these compounds although the same physical conditions are not realized (see ref. [21], Papoular).

In our approach, the feedback of the magnetic state on the lattice property is omitted. This coupling may be crucial; for example Andres *et al.* [14] have observed an abnormal thermal expansion of Al_3Ce below 0.70 K connected to a weak anomaly in the susceptibility. When the temperature is lowered, the compound seems to be successively in a paramagnetic state then in two magnetic long-range ordered states and finally in a non-magnetic state at 0 K. Further experimental results must elucidate this abnormal behaviour.

Finally we emphasize that our model contains only three physical parameters J , ρ and K_0 . The anisotropy term is essential to derive a strong coupling between the magnetic configurations.

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