Valence Fluctuating State in SmB6
T. Kasuya, K. Takegahara, T. Fujita, T. Tanaka, E. Bannai

To cite this version:

HAL Id: jpa-00218890
https://hal.archives-ouvertes.fr/jpa-00218890
Submitted on 1 Jan 1979

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Valence Fluctuating State in SmB$_6$

T. Kasuya, K. Takegahara, T. Fujita

Department of Physics, Tohoku University, Sendai, Japan

T. Tanaka and E. Bannai

National Institute for Researches in Inorganic Materials, Sakura-mura, Ibaraki, Japan

Résumé. — On a mesuré la chaleur spécifique et les propriétés de transport sur de bons monocristaux de SmB$_6$. Les mesures de chaleur spécifique montrent qu'il existe un gap en énergie de l'ordre de 100 K dans le système 4f, ce qui donne un très petit terme linéaire en $T$. Les mesures de conductivité indiquent que la conductivité usuelle de type hopping tend sans activation vers une valeur constante qui est cependant trois ordres de grandeur plus petite que ce que l'on croyait jusqu'ici être le minimum de conductivité métallique. On ne peut donc sûrement pas appliquer le modèle habituel de localisation d'Anderson que nous avions précédemment proposé. Nous proposons maintenant un modèle de formation d'un réseau de Wigner d'un type nouveau. Les propriétés anormales citées au-dessus sont expliquées dans ce modèle.

Abstract. — Specific heat and transport properties are measured on good single crystals of SmB$_6$. The specific heat experiment indicates that there is a gap of near 100 K in the 4f system leaving a very small $T$ linear term. Conductivity experiment indicates that the usual hopping type conductivity changes to a constant value without activation which is, however, three orders of magnitude smaller than the so far believed minimum metallic conductivity. The usual Anderson localization proposed before by us is clearly not applicable. Here, we propose a model of a new type of the Wigner lattice formation. Various anomalous properties mentioned above are explained within this model.

1. Introduction. — SmB$_6$ is known as one of the most typical valence fluctuating materials and much of experimental and theoretical works has been done so far. However, because of the difficulty to obtain well controled good single crystals and also due to the complicated unusual properties, it is not yet well established that what is the real intrinsic anomalous properties of this valence fluctuating state. In this paper, we present some of our recent experimental results on good single crystals of SmB$_6$ and propose a possible model to explain the results.

The typical characters of the valence fluctuating SmB$_6$ have been believed to be as follows [1]. (i) The ratio of $\text{Sm}^{3+}$ and $\text{Sm}^{2+}$ is about 0.6 $\sim$ 0.7 : 0.4 $\sim$ 0.3 and is nearly temperature independent. (ii) The valence is fluctuating in the time scale in between $10^{-8}$ and $10^{-15}$ s., probably around $10^{-13}$ s. (iii) The magnetic susceptibility is nearly explained by the 40% of singlet ground state $\text{Sm}^{3+}$ and the contribution from the magnetic $\text{Sm}^{4+}$ is nearly missed. (iv) The resistivity at room temperature is metallic but at low temperature it changes to the Mott type hopping. The thermoelectric power changes the sign twice. (v) The $T$-linear term of the low temperature specific heat is large reflecting a large 4f density of states at the Fermi level. (vi) Optical properties are very much different from the usual metals, in particular, large positive values of $\varepsilon_1$ were observed in the lower energy region [2]. These properties were explained by us before based on the extended Hubbard model and the Anderson localization for $\text{Sm}^{3+}$ states [3, 4]. However, as mentioned before, there remained some ambiguities in particular on (iv) and (v). More careful measurements have been done on these points and we have obtained results which are drastically different from the above mentioned properties.

2. Specific heat. — Specific heat of a good large single crystal of SmB$_6$ made by the floating zone method is shown in figure 1 together with these of LaB$_6$ and the non-magnetic part of EuB$_6$ [5], which are also made by the same method [6]. Because of the valence mixing state of SmB$_6$, we simply assume that the non-magnetic part of the specific heat of SmB$_6$ is the average of these of LaB$_6$ and EuB$_6$. Then the magnetic part of SmB$_6$ is obtained by subtracting it, which gives reasonable values of the entropy for 4f states, that is, 13 J/K mole at 75 K and 14.5 J/K mole extrapolated up to 120 K, in good agreement with the theoretical value,

$$8.31 \times (C_3 \ln 6 - C_3 \ln C_3 - C_2 \ln C_2) = 14.5 \text{ J/K mole}$$

for $C_3 = 0.6$, in which $C_3$ and $C_2$ are the concentrations of $\text{Sm}^{3+}$ and $\text{Sm}^{4+}$, respectively. It is
noticeable that the magnetic specific heat of SmB₆ begins near at 10 K and increases very rapidly with a broad peak at around 40 K. The overall feature is fairly well fitted by the Schottky type with the gap of about 100 K but the initial increasing part around 25 K in our experiment is sharper. The low temperature part of the specific heat is shown in figure 2 in the usual $C/T$ vs. $T^2$ plot together with other non-magnetic rare earth hexaborides [7]. The Debye specific heat of LaB₆ calculated from the sound velocity, that is, $\theta_d = 404$ K [8], is also shown for comparison. It is clear that the low temperature specific heat of RB₆ is much larger than that expected from the acoustic phonons. This is explained as follows [9]. The rotational motion of B₆ molecules becomes in phase for the wave vector on the edge of the cubic Brillouin zone, giving a very small phonon energy with an effectively two dimensional dispersion relation. This is responsible for the main part of the specific heat below 10 K because of its two dimensionality. In between 10 to 100 K, the optical phonons made by rare earth atoms and B₆ molecules become more important and above 100 K the internal B₆ molecular vibrations are most important. In YbB₆ and in ThB₆, the optical mode frequencies become lower and thus its contribution becomes significant even below 10 K. The proposed phonon spectra for LaB₆ are shown in figure 3. When the low temperature specific heat of SmB₆ is written as

$$C = \gamma T + C_{ph} + C_m,$$

it is clear that the phonon part $C_{ph}$ is similar to those of other hexaborides including LaB₆ in consistent with the conclusion mentioned before for the higher temperature region. Note that the rotational motion of B₆ seems to be not so much affected by the valency.
of rare earth atom. It is also seen that the tail of the main magnetic part \( C_m \) extends to about 8 K but not detectable below that temperature. A small hump at the lowest temperature may be due to some impurities. In the experiment done before by Nickerson et al. [10], the impurity term seems to be the dominant part in the lower temperature region. In our experiment, too, for less pure single crystals, we obtained a large impurity term. The \( \gamma \) value in our purest sample is 6.8 mJ/deg\(^2\) mole and is about twice that in LaB\(_6\) [11].

It is not clear whether this value still decreases further in purer sample. It is noticeable, however, that S. von Molnar obtained the nearly same value of \( \gamma \) on a small sample [12] which was made by us in a different method, plasma jet melting. Any way, the \( \gamma \) value is many orders of magnitude smaller than that which we expect from the narrow 4f bands at the Fermi level.

3. Transport. — Before, we reported [3] that the low temperature resistivity of pure single crystal SmB\(_6\) is described by Mott's \( T^{1/4} \) type hopping mechanism. To check it, the resistivity of the same sample has been measured down to 15 mK and we obtain the result that the resistivity is nearly constant below 100 mK. The same result, temperature independent resistivity in the lowest temperature region, is obtained also in other samples in which the constant value varies from 10 \( \Omega \) cm to 0.1 \( \Omega \) cm. It is possible to fit the data by the following form,

\[
\sigma = [0.143 + 29.4 \exp(-5.2/T^{1/4})] \quad (\Omega \text{ cm})^{-1}. \tag{2}
\]

This is the two channel model, the metallic [13] and Mott's type hopping channels. Note that, as shown in figure 4, the metallic and the simple exponential hopping channels model cannot fit the data so well as we reported before. In this model, the origin of the metallic channel is the problem, because the value of the present metallic conductivity is many orders of magnitude smaller than the so far believed minimum metallic conductivity [14]. Actually, in the present case, the mean free path should be many thousands times shorter than the atomic distance. One may argue that there may be some metallic phase at the surface. However, to explain the value 0.1 \( \Omega \) cm, many thousands layers should change to the metallic phase, which is too large. Actually, we could not detect such a metallic phase at the surface in any way and also it contradicts with our optical measurement in which the penetration depth is much less than such distance. As shown in figure 4, another form written by

\[
\sigma = 7.45 \exp[-19.3/(T+4.87)] \quad (\Omega \text{ cm})^{-1} \tag{3}
\]

can fit the experiment as well. This is the one channel model and is obtained by assuming that the activation energy \( \Delta \) decreases at low temperature proportionally to \( T \), that is, \( \Delta^{-1} \propto 1/(T_0/T) \), in which \( T_0 \) is a constant. It is clear that there are many other formulae to fit the experimental values as well. Any way, the present experiment indicates that transport phenomena in a strongly correlated many body narrow band system is very much different from those in one electron disordered system.

4. Theoretical models. — The above experimental results indicate clearly that the usual simple one electron picture on the Anderson localization and the hopping transport among them is not applicable in the present system. The most significant character of the present system is the existence of the energy gap about 50 to 100 K in the 4f system. Furthermore, this gap seems to be not induced by disorder but intrinsic, because the shape, or at least the initial sharp exponential increasing, of the main part of the magnetic specific heat is nearly sample independent.

A model calculation to induce an energy gap has been proposed recently by Sakai et al. [15]. Therefore, let us check their model at first. The Hamiltonian they used may be simplified as follows,

\[
\mathcal{H} = \sum_i E_i a_i^+ a_i + \sum_{\nu = 2, 3} \epsilon_{nm} C_{\nu}^+ C_{\nu} + \sum_I V(a_I^+ C_{\nu} + \text{c.c.}). \tag{4}
\]

It is assumed that, at each lattice point \( I \), there is a classical spin with a fixed direction \( \nu_I \) representing the spin state of divalent rare earth atom. \( a_I^+ \) represents the creation operator of an extra 4f electron at site \( I \), corresponding to the trivalent rare earth atom, in which the spin direction is allowed only for \( \nu_I \) by the Hund rule, while \( C_{\nu}^+ \) is the creation operator of the Wannier state for the conduction electron at site \( n \) and the spin direction \( \nu = \pm \) for a fixed common \( z \)-direction and the third term represents the s-f mixing. This model corresponds to the strong corre-
VALENCE FLUCTUATING STATE IN $\text{SmB}_6$

The phonon energy. Therefore, strong mixing among them is expected. With increasing temperature, the quasi-particles are

$\text{SmB}_6$, CS-31 1 translation limit for the 4f states but ignores the spin-orbit interaction and thus is not applicable to $\text{SmB}_6$ straight-forwardly, because the ground state of $\text{Sm}^{4+}$ is singlet due to the spin-orbit coupling. However, the essential physics may be represented by the above model [16]. Sakai solved the problem by using the CPA assuming perfect random orientation of the classical spin directions. However, it is clear that the ground state is not for such a randomly oriented state but an ordered state. Furthermore, for some ordered states, it is possible to solve Eq. (4) rigorously and thus to make the physical meaning clearer. Here, we assume the screw structure of the classical spins with a wave vector $\mathbf{Q}$. Then, Eq. (4) is rewritten by using the Fourier transformed operators

$$\mathcal{H} = \sum_k E_\mathbf{k} a_\mathbf{k}^+ a_\mathbf{k} + \sum_{k,n} \epsilon(k) C^+_k C_n +$$

$$+ \sum_k V(k) (C_k - Q/2 + C_k + Q/2) + \text{c.c.},$$

and then the solution is obtained by

$$(E - E_\mathbf{q})(E - \epsilon(k - \mathbf{Q}/2))(E - \epsilon(k + \mathbf{Q}/2)) =$$

$$= V^2(2E - \epsilon(k - \mathbf{Q}/2) - \epsilon(k + \mathbf{Q}/2)).$$

It should be noted that in the present treatment it is possible to treat the case in which the additional 4f electron has a transfer energy. Then, in Eq. (6), $E_i$ should be replaced by $E_\mathbf{k}(k)$. As shown in figure 5, for no dispersion of $E_\mathbf{q}$, we have an energy gap at the Fermi level $E_F$, which equals $E_i$ for one electron per site and $E_i$ lower than $E_\mathbf{q}$, or for two electrons per site and $E_i$ upper than $E_\mathbf{q}$. This means that the gap is easily formed for a large $Q$ and a small $E_F$. The amount of the energy gap is the order of $V^2/E_F$. Inserting the expected values, $V = 0.03$ eV and $E_F = 2$ eV; however, the energy gap is too small, much less than 1 meV. Furthermore, when the dispersion of $E_\mathbf{k}(k)$ is taken into account, as shown also in figure 5, even this small energy gap disappears. Therefore, the present model cannot be the main mechanism in $\text{SmB}_6$.

Here, we propose a new model, a new type of the Wigner lattice formation in a strongly correlated narrow quasi-band system. At first, let us consider the case of no randomness. Let us pick up $n$ highest energy quasi-band particles in the ground configuration and make the Wigner lattice with a lattice constant $R_n = n^{-1/3}$. Note that the Wigner lattice may be represented by a multiple directions large amplitude charge density wave state, in which the energy gap for the single particle excitation appears in any direction. The increase in the kinetic energy to form the localized states may be given by $\alpha_1 n^2/N(E_i)$ for nearly constant density of states $N(E)$, where $\alpha_1$ is a numerical constant of order unity. On the other hand, the decrease in the interaction energy due to this localization may be given by $-\alpha_2 n^2 U(E_i)$, in which $U(R)$ is given by averaging the interaction energy $I(r)$ to the distance $R$,

$$U(R) = \int_{R_0}^R I(r) \, dv \equiv U(\infty) f(R),$$

with $R_0$ being the crystal lattice constant. It is clear that $f(\infty) = 1$ and $f(R_0) = 0$ due to the strong correlation. Other terms, for example the change in the interaction form with $n$, are neglected. They may be included in $f(R)$. Then the formation of our Wigner lattice occurs in the condition

$$U(\infty) N(E_i) > \alpha_1/\alpha_2,$$

and $n$ is given by

$$n = \frac{2 U(R_n) N(E_i) - \alpha_1/\alpha_2}{N(E_i) \, dU(R_n)/dn}$$

in which $N$ is the number of lattice site. In $\text{SmB}_6$, the main term of $I(r)$ is expected to be the usual screened Coulomb interaction, while $N(E_i)$ is very large due to the narrow 4f band width, several hundreds in degree unit. Therefore, $U(\infty) N(E_i)$ is expected to be much larger than unity, probably near ten. Therefore, considerable amount of 4f electrons are expected to form our Wigner lattice.

Two kinds of excitation are expected in our Wigner lattice model. One is the single quasi-particle excitation with an energy gap $\Lambda$, which is of the order of $n/N(E_i)$. In $\text{SmB}_6$, $n$ is expected to be the same order as $N$ and thus $\Lambda$ is also the same order of the 4f band width, in consistent with our experiment of specific heat, $\Lambda \sim 100$ K. Another is the lattice vibration of our Wigner lattice. Because of the large effective mass of the 4f electrons, this vibration energy is estimated to be the same order as the crystal phonon energy. Therefore, strong mixing among them is expected. With increasing temperature, the quasi-particles are

![Fig. 5. Calculated dispersion curves are shown by the solid lines. (a) For a small Q value. (b) For a large Q value and (c) for a finite dispersion of $E_i(k)$](image-url)
excited more and the number of the localized electrons decreases. It causes the energy gap smaller and thus accelerates the process further. This seems to be the origin of the sharp increase of the specific heat in the $20 \sim 30 \, \text{K}$ region. It is interesting to see the critical region for the formation of the Wigner lattice. However, our Wigner lattice is influenced strongly by any imperfection and thus the critical region seems to be smeared out easily. In an imperfect crystal, our Wigner lattice will be distorted so much that it may be rather regarded as an amorphous type Wigner lattice. The quasi-particle excitation spectrum has tails now within the gap similar to the usual amorphous semiconductors, but the substantial amount of the energy gap is not expected to change much consistent with experiment mentioned before. On the other hand, from the analogy with the usual amorphous crystals, the collective modes may change so as to give the $T$ term in the specific heat at low temperature due to various nearly degenerated local structure. The amount of $\gamma$ in our SmB$_6$ is consistent with this model. Note that we cannot expect the $\gamma$ term from the conduction electrons because there is no density of states for the conduction electrons within the gap due to the d-f mixing effect [17].

In the next, let us consider the transport properties of our Wigner lattice system. At first, the mechanism to cause the minimum metallic conductivity is checked. In low temperature, the non-activated conductivity is given in one electron picture by [4]

$$\sigma = \pi e^2 \hbar N(E_F) \zeta(E_F),$$

where $\zeta(E_F)$ is the average of the square of the velocity matrix

$$\zeta_x(E_F) = \langle \langle s \mid v_x \mid s' \rangle \rangle_{E_x = E_F}.$$  

(11)

In one electron picture, when the density of states $N(E_F)$ is determined by the transfer energy, the transfer matrix is cancelled out by $\zeta$ part leaving a band width independent conductivity, while, when the potential fluctuation is so large that $N(E_F)$ is determined by the potential fluctuating energy, the Anderson localization occurs and thus no metallic conduction occurs. Therefore, the minimum metallic conductivity has strong correlation with the one particle Anderson localization in our Wigner lattice. In our Wigner lattice, we have always localized state by the many body effect. But for no randomness, the whole system is accelerated by the external field in the way similar to the free 4f band state. With random potential, our amorphous Wigner lattice is locally pinned by the potential but can move by tunneling to another configuration with the similar energy which is seen by the $T$ linear term of the specific heat. The essential difference from the one particle picture is as follows. In the present case, an energy difference of one particle jump is compensated by correlated successive jumps in many other sites, which is thus of nearly continuous spectra and thus support the non-activated process. It may be possible to translate the above situation into a one electron picture as follows. The density of states $N(E_F)$ of the effective impurity states is given by the $\gamma$ value in the usual way, which is about two orders of magnitude smaller than that of the narrow 4f bands, while the $\zeta$ part in Eq. (11) is also smaller than that expected from the bare 4f bands because, accompanied with a major one electron transfer, many other electrons also make smaller jumps to adjust themselves to the change caused by the major jump self-consistently. Therefore, we expect that the metallic conductivity of our system is at least the factor $(\gamma/\gamma_{4f})^2 \sim 10^{-2}$ smaller than the usual minimum metallic conductivity, the order of $10^{4}$ (A cm)$^{-1}$, in good agreement with our experiment shown before. Furthermore, our experimental results that the impure sample with a larger $\gamma$ value has a larger metallic conductivity also support the present model. As temperature rises, the phonon assisted transfer process to a state with a higher energy but a larger transfer matrix becomes more important, which is similar to the usual hopping process with an activation energy, and for higher temperature, the contribution of the thermally activated single particle 4f electrons above the gap becomes most important. These 4f states are expected to be given by the Anderson localization state as was proposed before. It is clear that in the region outside of the mobility edge, the contribution of the conduction electrons is most important. The complicated temperature dependences of the electrical resistivity and the thermoelectric power of SmB$_6$ are explained just on this model [18]. The detail will be published elsewhere and here we point out some important characters related with the above mentioned 4f states.

The temperature dependence of the electrical resistivity above 5 K is given approximately by the exponential type with the activation energy $E_c$ of about

\[ \mu(T) = \mu_0 \exp \left( \frac{T_c - T}{T} \right)^{1/2} \]

for $T < T_c$, where $\mu_0$ is the room temperature mobility and $T_c$ is the critical temperature. The data for $C_p$ and $\mu$ are shown in Figs. 6(a) and 6(b), respectively. The solid lines in these figures are the calculations using the model described above.
VALENCE FLUCTUATING STATE IN SmB₆

50 K. This is entirely due to the conduction electrons outside of the mobility edge. More detailed measurements [19] show, however, some fine structure, which is well described by the temperature dependence of the Fermi level \( E_F \) as shown in figure 6a. There are practically no arbitrary adjustable parameters. Note that the phonon scattering is negligibly small, less than 10% of the total scattering. The temperature dependence of the thermoelectric power is more sensitive to the detailed structure of the 4f states. A nearly temperature independent small positive value in higher temperature region as shown in figure 6b is explained naturally only when we take into account the excited 4f multiplets of both Sm⁺⁺ and Sm⁺⁺⁺. When we consider only the contributions from the conduction electrons and the 4f states in the collective mode, the minimum of the thermoelectric power becomes very small, -600 \( \mu \)V/K at 10 K. Experimentally, this minimum depends sensitively on samples and in our experiment ranges between -100 to -40 \( \mu \)V/K. This is explained only by considering the thermally excited individual 4f states mentioned before. Note that except the fine structure, our experiments on resistivity and thermoelectric power are consistent in overall feature with the preceding experiments [10, 20].

5. Concluding remarks. — Measurements of the specific heat and the electrical resistivity on pure single crystals of SmB₆ have revealed that the simple one particle Anderson localization model of the strongly correlated narrow 4f quasi-band proposed before by us [4] is not applicable. We proposed here a new model, a new type of the Wigner localization, in which only a part near the Fermi energy participates to form our Wigner lattice. Expected electronic and transport properties are reviewed briefly semiquantitatively. Although there are some conjectures on the theory, the proposed model seems to be a hopeful candidate to explain various anomalous properties of the valence fluctuating state in SmB₆ consistently.

References

[5] The detail for the EuB₆ data will be published in other paper.
[9] The detail will be published in other paper.
[11] As seen in figure 2, the \( \gamma \) value in LaB₆ depends on sample.

This seems to be mostly due to the sensitive dependence of the in-phase rotational phonon mode on defects.

[13] Here we use the word metallic in the sense that there is no effective activation energy.
[16] It is possible to release the restriction of the classical spin model for divalent state and also to include effect of spin-orbit coupling. Private communication by Sakai, O.
[17] The detailed calculation on the properties of our Wigner lattice system will be published in the forthcoming paper.
[18] Fitting of these properties was done before in ref. [10]. For it, they used many narrow bands with many parameters, but there are no physical reality on these bands.
[19] To be published.