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MIXED VALENT SEMICONDUCTORS : SmB_6

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Résumé.— Nous présentons des arguments expérimentaux et théoriques étayant l'hypothèse que SmB_6 est un semiconducteur de valence uniformément mixte (c'est à dire de valence intermédiaire et aux sites équivalents). Il est souligné que les expériences sur propriétés de transport impliquent que la surface de Fermi est soit extrêmement petite, soit non-existante. Des considérations théoriques générale indiquent la possibilité de l'existence d'un gap situé au niveau de Fermi.

Abstract.— An overview is given of the experimental and theoretical evidence that SmB_6 is a homogeneously mixed valent semiconductor. It is emphasized that the experimental transport properties imply that the Fermi surface is either extremely small or non-existent, and that rather general theoretical considerations support the possibility of a gap at the Fermi level.

1. Introduction and perspective. — The temperature dependence of their resistivity divides homogeneously mixed valent rare earth compounds into two groups /1/, those like CePd_3 whose low temperature resistivity falls nearly to zero with decreasing temperature /2/ and those like SmB_6 whose low temperature resistivity becomes very large with decreasing temperature. The members of the former group are correctly regarded as metals. Of the members of the second group, which also includes the gold phase of SmS and the antiferromagnetic phase of TmSe , only SmB_6 has ever been modeled as a semiconductor, and the existence of any homogeneously mixed valent insulators has remained a controversial topic in the field of mixed valence. The history of this subject is reviewed briefly in this section.

The temperature dependence of the resistance of SmB_6 was reported in 1969 by Menth et al. /3/. They found a low temperature resistance rise of a factor of 10^3 , exponentially activated with energy 2.5 meV between 4K and 15K, and suggested that SmB_6 was a semiconductor in which Sm was present as Sm^{2+} and that the activation energy was that required to promote a 4f electron to the conduction band. This model was disproved in 1970 by Cohen et al. /4/ who reported that the Sm isomer shift in the Mössbauer spectrum implied temperature independent valence mixing between 4K and 300K. They suggested that the electron liberated from the 4f shell in valence mixing remained bound to a Sm^{3+} site at low temperature but did not elaborate on the increased conductivity at higher temperature. In 1971, Nickerson et al. /5/ reported the temperature dependence of the resistivity and Hall coefficient

in SmB_6 . They interpreted the data in a three-band model which included a small gap between localized and delocalized states. The localized states had a complex character involving bound 5d-electrons in order to interpret the Mössbauer and magnetic susceptibility data. They also reported a fairly large linear specific heat which was attributed to carriers in an impurity band. Mott /6/ in 1973 introduced a hybridized 4f-5d band picture with a gap at the Fermi level. He also attributed the linear specific heat to an impurity band.

Over the same time period, studies of valence mixing due to pressure or alloying in Sm chalcogenides were made. The mixed valence state was obtained from a state of definite semiconductor character, and was generally regarded as metallic, in spite of small low temperature resistance rises in some cases.

With the emergence of mixed valence as a more cohesive field there was a tendency to try to develop a unified model valid for all compounds. Many mixed valent compounds were obviously metallic with large linear specific heats indicative of a large density of states at the Fermi level. Further it became clear that the properties of mixed valent compounds were quite sample-dependent, making it plausible to dismiss the resistivity rise in some of them as an extrinsic effect of some sort. In his 1976 review, Varma /7/ argued against a gap to explain the resistivity rise, citing the non-zero γ -term in the specific heat, and also the non-zero $T=0$ magnetic susceptibility. Also in 1976, Kasuya /8/ proposed that the large low temperature resistivity in SmB_6 was due to Anderson localization of

states at the Fermi energy, but that perfect SmB_6 would be a metal.

At the 1977 Mixed Valence Conference in Rochester, the metallic model was widely used. Varma /9/ advanced as a general model of the mixed valent ground state the two component Fermi liquid. Kasuya /10/ enlarged on his hopping picture for SmB_6 and analyzed the low temperature resistivity with a $T^{-1/4}$ law. Tournier and his co-workers ascribed the low temperature resistance rise in several mixed valent rare earth chalcogenides to Kondo scattering from magnetic impurities /11,12/.

The possible existence of homogeneously mixed valent semiconductors was reexamined in a 1978 paper by Allen, Martin, Batlogg and Wachter /1/, in the context of analyzing the semiconductor-like room temperature infrared optical properties of SmB_6 and the gold phase of SmS , which had been reported at the Rochester Mixed Valence Conference /13,14/. They stated, but without discussion, that the low temperature resistivity in SmB_6 was so large it implied a mean free path much less than the lattice constant, and therefore could not be easily dismissed. They also pointed out that specific heat measurements had not then been made on samples of SmB_6 with a large low temperature resistivity rise and that measured γ 's were smaller in samples with higher low temperature resistivities.

2. Thermal, Electrical and Optical Properties of SmB_6 .

2.1. Resistivity and Specific Heat in $\text{Sm}_{1-x}\text{B}_6$.

Both the resistivity and specific heat of SmB_6 samples have been found to be sample dependent, almost certainly due to variations in stoichiometry, as shown by systematic studies of $\text{Sm}_{1-x}\text{B}_6$ /10/. Samples with x closest to zero show the largest low temperature resistivity rise, nearly a factor of 10^4 , and the lowest room temperature resistivity. In all samples the resistivity rise saturates below a temperature which is lowest for x closest to 0. The first measurements reported on the low temperature specific heat /5/ of SmB_6 showed it to be not precisely linear with temperature, there being a bump reminiscent of a Schottky anomaly, but γ values for two samples could be estimated to be 30 mJ/mole K^2 , and 80 mJ/mole K^2 . The smaller γ was found in the sample with the higher low temperature resistivity. Recently Kasuya and co-workers /15/ have reported a γ of 6.8 mJ/mole K^2

for samples with x nearly zero. In addition, there was around 40K a broad peak having the overall features of a Schottky anomaly. The value of γ is about twice that of LaB_6 , but is very much smaller than that which would be expected from a narrow 4f band at the Fermi level /15/. These most recent specific heat results mitigate against a simple heavy Fermi liquid picture of the 4f electrons in SmB_6 , and suggest the presence of a gap in the electronic states.

2.2. Resistivity of SmB_6 .— The discussion of the resistivity of nearly stoichiometric SmB_6 proceeds most easily with certain principles clearly in mind. For weak scattering in a Fermi liquid, the conductivity σ is proportional to the mean free path L of electrons at the Fermi level. In the absence of any disorder, L and the conductivity become infinite as the temperature $T \rightarrow 0$, the behavior of a perfect Fermi liquid. For a Fermi liquid with static disorder the conductivity is finite as $T \rightarrow 0$, but Mott /16/ has argued that there is a lower limit $\sigma_{\min}$ on its value. The existence of this limit is motivated by the expectation that L has a lower limit given by $k_F L \sim \pi$, where k_F is the Fermi wavevector /17/. For a metallic number of carriers, k_F is $\sim \pi/a$, so the condition is $L \geq a$, where a is the interatomic spacing. Mott /16/ has identified the regime where disorder would induce L to be much less than the interatomic spacing with disorder-induced Anderson localization /18/. If the disorder causing the localization is static, the conductivity at $T = 0$ is expected to be zero, which can be taken to define localization. For $T > 0$ the conductivity in states localized by static disorder need not vanish because thermally activated hopping may occur. At any temperature an experimental conductivity much less than $\sigma_{\min}$ or small enough to imply $L \ll a$ for a metallic number of carriers means either that the transport proceeds via localized states or that the number of carriers is much smaller than that of a typical metal.

The value of $\sigma_{\min}$ can be estimated in various ways which give similar order-of-magnitude results. Applying /19/ one of these, known as the unitarity limit /20,21/, yields a maximum resistivity $\rho_u = 544 \mu\Omega \text{ cm}$ for SmB_6 /22/, assuming a density of carriers equal to the average number of Sm^{3+} ions,

$8.5 \times 10^{21}/\text{cm}^3$. It can be shown that L is approximately the lattice constant for this estimate.

The temperature dependence of the resistivity of a nearly stoichiometric sample of SmB_6 /22/ is shown in Figure 1.

Fig. 1 : Temperature dependence of resistivity of SmB_6 .

At 300 K, ρ is $290 \mu\Omega \text{ cm}$, not much less than the value of ρ_u and implying $L \sim a$. As the temperature decreases the resistivity rises to a value of $2.6 \Omega \text{ cm}$ at 4K, about 5000 times larger than the value of ρ_u . For this resistivity, assuming a metallic number of carriers equal to the average density of Sm^{3+} ions, one deduces /22/ from standard formulas that $L = 2.8 \times 10^{-4} \text{ X } a$, an impossible value. The conclusion is that the resistivity rise must be ascribed to a decrease of carriers relative to that at room temperature or to conduction in states localized by disorder.

A conductivity decrease due to disorder was considered by Kasuya /8,10/, who proposed that perfect SmB_6 would be a metal, but that disorder due to small numbers of Sm vacancies caused the states at the Fermi level to be Anderson localized. Two experimental results disagree with this explanation. One /1/ is that deliberate introduction of vacancies increases, rather than decreases, the low temperature conductivity /10/. The second, pointed out by Kasuya /15/, is that measurements by he and his co-workers of the conductivity down to 15 mK show the

conductivity to saturate rather than fall to zero. Assuming this behaviour extends to $T = 0$, it must be concluded that in the samples measured to date hopping transport does not occur at the lowest temperatures and that nonlocalized states exist at the Fermi energy. In the next section the Hall effect is used to estimate carrier densities at high and low temperatures.

2.3. Hall Effect for SmB_6 . - The temperature dependence of the Hall coefficient R_H /22/ for the sample yielding the data of figure 1 is shown in figure 2.

Fig.2 : Temperature dependence of the Hall coefficient of SmB_6 .

Comparing to data taken on less stoichiometric samples /5/, there are significant differences at low temperatures, and the following pattern emerges. As sample stoichiometry improves, the size of the low temperature resistivity rise and the magnitude of the negative R_H peak increase together, while the temperature at which the resistivity rise saturates and the temperature of the maximum in R_H decrease together. In contrast to the data of figure 2, for a sample with a resistivity rise of only 1.5 orders of magnitude, the negative peak occurs at 12K with a magnitude of only $0.04 \text{ cm}^3/\text{C}$ and below 12K R_H abruptly turns toward zero, becoming positive below 5K /5/. The small positive values of R_H between $\sim 60\text{K}$ and 300K show little sample dependence. A summary of an analysis /22/ of the data of figure 2 is given below.

A detailed analysis of the temperature

dependence of R_H is not possible in the absence of a detailed model of the electronic structure of SmB_6 . But estimates of carrier concentrations at high and low temperatures can be made unless the Hall and drift mobilities are not comparable, as happens in the anomalous Hall effect or for hopping conductivity. A large anomalous Hall effect seems unlikely for SmB_6 because it does not order magnetically and its magnetic susceptibility is small, with a weak temperature dependence compared to that of R_H . The arguments against hopping conductivity have been given above.

Since R_H changes sign with temperature variation, the simple two parabolic-bands model has been used to estimate carrier densities. It can be shown /22/ that in this model upper bounds on the densities of holes and electrons follow simply from placing a lower limit on the mobility of the carrier which does not determine the sign of R_H . This limit was chosen as that corresponding to the resistivity ρ_u , and is equal to $1.35 \text{ cm}^2/\text{V sec}$. For room temperature the analysis gives carrier densities $\sim 9 \times 10^{21}/\text{cm}^3$, and mobilities $\sim 1.8 \text{ cm}^2/\text{V sec}$; at 4K the carrier densities are less than $\sim 5 \times 10^{17}/\text{cm}^3$ and the mobilities are in the range $2\text{--}40 \text{ cm}^2/\text{V sec}$.

The room temperature carrier density is very close to the average number of Sm^{3+} sites, and the mobility and resistivity are close to the unitarity limit values, leading to a picture of SmB_6 at room temperature as a poor metal. As the temperature decreases the number of carriers decreases by a factor of $\sim 10^4$, causing the conductivity to decrease by a factor of $\sim 10^4$. Such behavior is compatible with a small gap semiconductor model (or possibly a semi-metal model with a very narrow density-of-states minimum), and activation energies of about 1.8 meV and 2.7 meV can be deduced from, respectively, plots of $\log |R_H|$ and $\log \rho$ vs. $1/T$, in the temperature range 4K–13K. A gap the order of magnitude of these activation energies is consistent with the Schottky type specific heat anomaly, and with the bad metal behavior at room temperature, where kT is about 10 times larger than the activation energy /6/.

2.4. The Residual Conductivity.— As emphasized by Kasuya /15/ it is important to assess whether the residual conductivity is consistent with estimates

of minimum metallic conductivity. Using /22/ the low temperature carrier density deduced from the Hall effect to estimate the characteristic length in an expression given by Mott /23/ for $\sigma_{\min}$ yields $\sigma_{\min} = 5.7 (\Omega \text{ cm})^{-1}$, about 15 times the observed conductivity of $0.38 (\Omega \text{ cm})^{-1}$. Given the general difficulty of assessing $\sigma_{\min}$ /23/ and the lack of detailed knowledge of the states at the Fermi energy, it is by no means clear that a factor of 10 is cause for alarm.

Kasuya /15/ has compared the observed conductivity with a much larger estimate of $\sigma_{\min}$, appropriate for a metallic number of carriers, and argued that a novel model of the ground state is required to evade the conflict. To this end, he has proposed that a gap exists at the Fermi energy due to the formation of a Wigner lattice. In the absence of disorder the conductivity would be infinite at $T = 0$ due to phase slippage of the lattice. Disorder pins the lattice and reduces the conductivity to the observed value. Again it is appropriate to point out that the experimental fact that the conductivity increases with degraded stoichiometry mitigates generally against any models in which defects reduce otherwise infinite conductivity. Also Kasuya's estimate of $\sigma_{\min}$ is unnecessarily large, as shown above.

Nonetheless, the issue of the residual conductivity and especially its relation to the residual linear specific heat requires further experimental and theoretical consideration.

2.5. Optical Properties.— The optical conductivity /1/ of SmB_6 for temperatures between 300K and 4K is that of a metal at photon energies greater than $\sim 0.5 \text{ eV}$, and there is a temperature independent /13/ plasma edge in the optical reflectivity at $\sim 1.5 \text{ eV}$. It is to be emphasized that a small gap at the Fermi level will not affect the high energy dielectric response, and that the energy of the reflectivity edge has no automatic relation to the carrier density involved in d.c. transport. Assertions to the contrary /24/ are incorrect. At room temperature the optical properties of SmB_6 between 0.02 and 0.5 eV are insulator-like in that the real part of the dielectric constant becomes large and positive at low energy, but this behavior can be accounted for in the bad-metal model valid at high temperatures /1/. Low temperature, low

frequency spectroscopy in the meV range, which could reveal details of the energy levels near the Fermi energy, remains to be done.

3. Theory of the Hybridization Gap.— Mott's proposal /6/ of a 4f-5d band model with a hybridization gap at the Fermi level left open two questions, whether simple well-defined bands are appropriate to describe the interacting 4f electrons, and if so, whether a gap is likely to occur for a realistic band structure. Both of these questions have been addressed in a recent theoretical study /25/. There is space here to summarize only the most salient points of the theory, as follows.

(a) SmB_6 is cubic with Sm ions at sites with full O_h symmetry. Symmetry arguments show that there is an isolated, lowest-energy, fermion hole excitation in which an electron is removed from a Sm^{2+} ion in its ground $J = 0$ state to create a Sm^{3+} ion in the lowest energy state split off from the ground $6H_{5/2}$ configuration by the cubic crystal field. This excitation is a doublet, transforming as Γ_7^- in O_h , and a single such excitation results in a well-defined band.

(b) Band calculations for LaB_6 /26/ show that in SmB_6 the Fermi level will lie in an isolated band, which is orbitally nondegenerate except at Γ and which has its minimum at the X-point. For homogeneous mixed valence, the Fermi level must also intersect the 4f excitation described in (a).

(c) It happens that this band and the 4f excitation have the same symmetry throughout the Brillouin zone, except at Γ . Were there not strong Coulomb interactions of the dense number of f holes with each other or with the band electrons, then there would be a gap if the 4f band had zero or positive dispersion from Γ to X, and counting electrons shows that the Fermi level would lie in the gap. This situation is shown in Figure 3(a).

(d) Including the Coulomb interactions the problem for the states closest to the Fermi level is equivalent to a two-band Hubbard model in which the site occupations for the narrow f-band are either one or two. Solving for the one-particle Green's function using the decoupling approximations of Hubbard III /27,28/ shows that, if the narrow band occupation n_f is not too close to one, the gap in the density of states remains, even though two major changes in the simple band picture

occur. These changes, shown in figure 3(b), are that a portion of the occupied density of states is split off to lower energies by U , the 4f hole-hole Coulomb interaction, and that the f-states suffer strong Coulomb scattering which decreases the gap and induces uncertainty in k . Very near the band gap this uncertainty is an artifact of the calculation, but away from the gap it is real. The details of the conditions for gap existence and other features of the solution are described elsewhere/25/.

Fig. 3 : Schematic band diagram for SmB_6 . (a) Simple bands for lowest energy $\text{Sm } f^6 \leftrightarrow f^5$ transition and conduction band as determined in Ref. /26/. (b) Including large f-f Coulomb interaction, as discussed in text.

(e) If there is an even integral number of electrons per atom, then the Fermi level remains in the gap for all cases in which the gap exists, in spite of the altered density of states. That this is so can be regarded as a consequence of the Luttinger theorem /29/ which states that turning on Coulomb interactions does not alter the volume enclosed by the Fermi surface provided that there is no change of symmetry and that no states cross the Fermi energy. The gap itself is most easily understood by considering the mixed valent states as an analytic continuation from the integral valent state in which the Fermi level is in a gap between the filled $4f^6$ states and the unoccupied broad 5d-band. That the integral valent state for Sm is the nondegenerate $4f^6$ $J = 0$ configuration is of obvious central importance in the application of these two general ideas.

4. Other Compounds.— Other compounds of interest

are SmS, whose mixed valent phase shows a modest low temperature resistivity increase /30/, and TmSe, whose resistivity is high in its antiferromagnetic phase, but low in its ferromagnetic and paramagnetic phases /31,32/. Band calculations for insulating SmS show that electrons liberated from the 4f shell will occupy a singly degenerate band with a minimum at the X-point. This band has the same symmetry as the f-band except at the Γ and X points, implying the possibility of a very small Fermi surface. TmSe presents additional complications because the mixed valence state involves Tm^{2+} ($4f^{13}$) with $^2F_{7/2}$ ground state and Tm^{3+} ($4f^{12}$) with 3H_6 ground state, each of which is degenerate. The results of Ref./25/ suggest that a gap is unlikely in a ferromagnetic mixed valence state, whereas a gap is not obviously precluded in the antiferromagnetic phase.

5. Summary.— In summary, the following points should be emphasized for SmB_6 .

(a) The experimental properties imply a Fermi surface that is either extremely small or non-existent, and are completely inconsistent with a model of the 4f electrons as a heavy Fermi liquid of metallic density.

(b) Rather general theoretical considerations show that homogeneously mixed valent SmB_6 can have a gap at the Fermi level.

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