

## Large low-temperature Hall effect and resistivity in mixed-valent $\text{SmB}_6$

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The Hall coefficient  $R_H$  has been measured between 2 and 300 K for small crystals of  $\text{SmB}_6$  in which the resistivity  $\rho$  at 4 K is nearly  $10^4$  times greater than its 300-K value of  $290 \mu\Omega \text{ cm}$ . Significant differences from previous results reported for samples with a much smaller low-temperature resistivity rise have been found. It is shown that the size of the resistivity increase precludes its being ascribed to a scattering mechanism for a metallic number of carriers, and that the size of  $R_H$  implies numbers of holes and electrons less than  $\sim 5 \times 10^{17}/\text{cm}^3$  at 4 K. The origin of the low-temperature residual conductivity is discussed.

### I. INTRODUCTION

$\text{SmB}_6$  is one of a group of homogeneously-mixed-valent materials in which the resistivity increases with decreasing temperature.<sup>1,2</sup> Because it is often stated<sup>3</sup> that in general the mixed-valent state has a metallic Fermi-liquid character, and because many mixed-valent materials are clearly metallic, this group, which also includes  $\text{TmSe}$  and high-pressure  $\text{SmS}$ , has provoked questions as to whether the resistivity rise is an intrinsic property of these mixed-valent materials, and whether the rise should be ascribed to a scattering mechanism or to a carrier decrease.

In  $\text{SmB}_6$  the resistance increase is rapid below 30 K, saturates at some lower temperature, and then is nearly constant down to the lowest temperature of measurement. The behavior is quantitatively sample dependent, probably due to variations in stoichiometry, as shown by systematic studies of  $\text{Sm}_{1-x}\text{B}_6$ .<sup>4</sup> Samples with  $x$  closest to 0 show the largest resistivity rise, nearly a factor of  $10^4$ , and the lowest saturation temperature, about 3 K. As  $x$  increases from 0, the size of the resistivity rise decreases and the saturation temperature increases. Only one Hall-effect study has been reported for  $\text{SmB}_6$ ,<sup>5</sup> and this was made on samples in which the resistivity rise is less than 2.5 orders of magnitude and the saturation temperature is higher than 6.5 K. Comparison with the resistivity studies on  $\text{Sm}_{1-x}\text{B}_6$  then suggests that the reported low-temperature Hall-coefficient behavior is not characteristic of stoichiometric  $\text{SmB}_6$  and that measurements of the Hall coefficient in material with a much larger resistivity rise might reveal significant differences. Such has been found to be the case.

The remainder of this paper describes the new Hall-effect measurement and points out differences from the previous results. It is shown that the resistivity increase is too large to be ascribed to scattering of a metallic number of carriers and that the size of

the Hall coefficient  $R_H$  implies a number of carriers less than  $\sim 5 \times 10^{17}/\text{cm}^3$  at 4 K. The origin of the residual conductivity is discussed.

### II. EXPERIMENTAL RESULTS

The Hall coefficient and resistivity were measured at 230 Hz by the four-terminal Van der Pauw method.<sup>6</sup> A signal generator was used as a current source and a lockin amplifier was used to detect the voltage. Electrical isolation between the voltage and current circuits was achieved through shielding and by using an optical coupler to provide a reference signal to the lockin amplifier from the signal generator. The current was determined by measuring the voltage across a calibrated series resistor with the lockin amplifier. The magnetic field strength for the Hall measurement was 17 kG.

The samples of  $\text{SmB}_6$  were small, thin flux-grown crystalline flakes provided by Z. Fisk of the University of California at LaJolla. The dimensions of the sample for which data is presented were  $0.55 \text{ mm} \times 1.1 \text{ mm} \times 40 \mu\text{m}$ . Contacts were made to the corners of the sample with  $100\text{-}\mu\text{m}$ -diameter Beryllco wires whose tips were sharpened by electroetching to points about  $10 \mu\text{m}$  in diameter. The wires were soldered to terminals on one side of a thin insulating plate and bent to protrude through four carefully positioned  $150 \mu\text{m}$  holes to contact the sample, which was mounted on the opposite side of the plate. The sample was held in place by a thin piece of quartz pressed on by a small wire spring clip, and the contact wires were shaped to press against the sample under tension. These contacts were found to be reversible and ohmic using a curve tracer oscilloscope. Occasional lapses of contact quality during the course of the measurements could be cured by discharging a capacitor through the contacts.

Figure 1 shows the resistivity  $\rho$  between 2 and 300

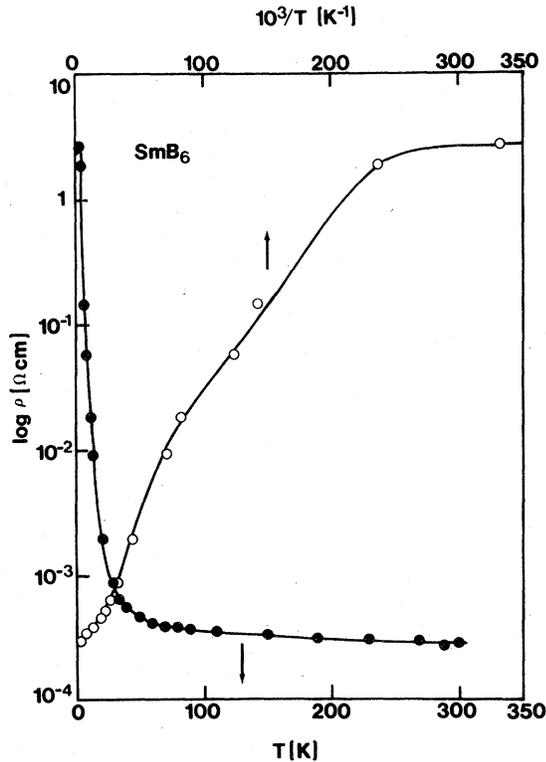


FIG. 1. Temperature dependence of resistivity of  $\text{SmB}_6$ .

K. The size of the low-temperature increase is nearly a factor of  $10^4$  and its saturation temperature is about 3 K, indicating that the sample is close to being stoichiometric. The temperature dependence of the Hall coefficient is presented in Fig. 2. Between 300 and 58 K  $R_H$  is positive and never larger than  $10^{-3} \text{ cm}^3/\text{C}$ . Below 58 K  $R_H$  is negative, its magnitude increasing strongly between 58 and 4 K to a value near  $30 \text{ cm}^3/\text{C}$ , and then decreasing slightly between 4 and 2 K.

Above 57 K the values of  $R_H$  are very similar to those reported previously by Nickerson *et al.*,<sup>5</sup> except that the high-temperature zero crossing occurs 3–5 K higher in the previous data. However, there are striking differences from the previous data at lower temperatures. For a sample with a low-temperature resistance rise of about 1.5 orders of magnitude, Nickerson *et al.* found that  $R_H$  was negative with a magnitude that increased to a peak value of  $0.04 \text{ cm}^3/\text{C}$  around 12 K and then decreased sharply as the temperature was lowered further, so that a low-temperature zero crossing to positive values occurred at about 5 K. The temperature of the peak in  $|R_H|$  was just above the temperature,  $\sim 10$  K, at which the resistivity rise began to saturate in this sample. For a second sample with a larger low-

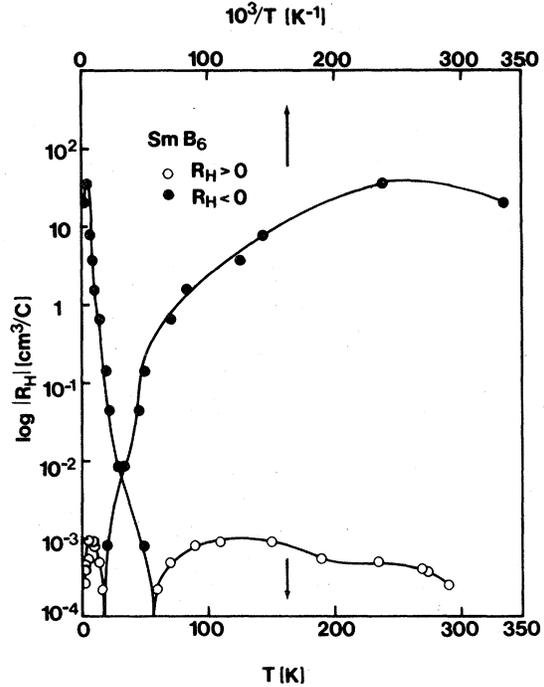


FIG. 2. Temperature dependence of the Hall coefficient of  $\text{SmB}_6$  measured with  $B = 17 \text{ kG}$ .

temperature resistivity rise, about 2.5 orders of magnitude,  $R_H$  was qualitatively the same but with interesting quantitative differences. The maximum in the magnitude of  $R_H$  occurred at about 8.5 K, with a larger value, about  $0.85 \text{ cm}^3/\text{C}$  (for this sample  $\rho$  and  $\mu_H$  were published so  $R_H$  has been deduced with some uncertainty, from the relation  $R_H = \rho \mu_H$ ). Again the temperature of the peak in  $|R_H|$  was just above the resistance rise saturation temperature, about 6.5 K in this sample. The low-temperature zero crossing to a positive value is at a slightly higher temperature than in the first sample, near 6 K.

Taking previously published data together with the new data presented in Figs. 1 and 2, the following pattern emerges. As sample stoichiometry improves, the size of the low-temperature resistance 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 the data of Fig. 2 the low-temperature zero crossing of  $R_H$  to a positive value does not even occur. This strongly suggests that the saturation of  $\rho$  is correlated with the peaking of  $R_H$  and that both are extrinsic. Similarly it appears that a large magnitude of  $R_H$  accompanies a high value of  $\rho$ , and both are intrinsic.

### III. DISCUSSION

#### A. Minimum metallic conductivity, the unitarity limit, and the failure of the scattering model

Consider now the low-temperature increase of the resistivity. It is the aim of this section to show that the resistivity reaches a value too large to be accounted for by scattering of a metallic number of electrons in delocalized states and to that end lower limits on metallic conductivity will be discussed. The expression for the conductivity  $\sigma$  obtained from the Boltzmann equation for a metallic cubic crystal is<sup>7</sup>

$$\sigma = \frac{e^2}{\hbar} \frac{S_F}{12\pi^3} L, \quad (1)$$

where  $S_F$  is the Fermi-surface area and  $L$ , the mean free path, is  $v_F \tau$  where  $v_F$  and  $\tau$  are, respectively, the velocity and lifetime of electrons at the Fermi level. Strictly,  $L$  in Eq. (1) is the mean free path averaged over the Fermi surface if the surface is not spherical, but it is assumed here that the electrons are in a parabolic band. This assumption leads to simple results that display important qualitative relationships and does not introduce numerical error large enough to invalidate the order-of-magnitude comparisons to be made. For a parabolic band  $v_F$  is related to the effective mass  $m^*$  and the Fermi wave vector  $k_F$  by  $m^* v_F = \hbar k_F$ . Using this relation and putting  $S_F = 4\pi k_F^2$ , Eq. (1) takes the often used form  $\sigma = ne\mu$  where  $n = k_F^3/3\pi^2$  is the conduction-electron density and  $\mu = e\tau/m^*$  is the mobility. It follows that the mobility and mean free path are related by

$$L = \frac{\hbar}{e} k_F \mu = \hbar k_F \frac{\tau}{m^*}. \quad (2)$$

In the absence of any disorder, static or thermal,  $\tau$  and  $L$  are infinite, so for a system without static disorder,  $\tau$ ,  $L$ , and the conductivity become infinite as the temperature  $T \rightarrow 0$ . This is the behavior expected of a perfect Fermi liquid. For a Fermi liquid with static disorder, the conductivity is finite as  $T \rightarrow 0$ , but Mott<sup>8</sup> has argued that there is a lower limit  $\sigma_{\min}$  on its value. That this is so can be motivated by the idea that there is a lower limit on  $L$ . As pointed out by Ioffe and Regel,<sup>9</sup> and discussed extensively by Mott,  $L$  is expected to obey the inequality  $k_F L > \pi$ . For a metallic number of carriers  $k_F$  is approximately  $\pi/a$ , where  $a$  is the interatomic separation, so the condition is equivalent to  $L > a$ . Mott<sup>8</sup> has identified the regime where disorder would induce  $L$  to be much less than the interatomic separation with disorder-induced Anderson localization.<sup>10</sup> 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. It may also happen that thermal disorder is responsible for inducing localization, in which case the conductivity at  $T=0$  should be greater than  $\sigma_{\min}$ , whatever its value when  $T > 0$ . An experimental conductivity 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.

For a system which may have unusually narrow bands at the Fermi level, as with mixed valence, it is important to assess the role of  $m^*$ , which will be large for narrow bands. Since  $k_F$  does not change for a simple variation of the bandwidth, Eq. (1) shows that  $\sigma$  depends on  $m^*$  through  $L$ , and Eq. (2) shows an explicit inverse dependence of  $L$  on  $m^*$ , reflecting the fact that heavier electrons have a smaller  $v_F$ . In addition  $\tau$  is proportional to an inverse scattering rate, which is typically proportional to the density of states at the Fermi level, causing  $\tau$  to vary inversely with  $m^*$ . Thus  $L$  is typically proportional to  $m^{*-2}$  so a large  $m^*$  is expected to make  $L$ , and hence  $\sigma$ , small. However, in a Fermi-liquid model, a very small conductivity cannot be accounted for simply by invoking a sufficiently large  $m^*$  if this leads to  $L \ll a$ . Large  $m^*$  systems are not exempt from the ideas of the preceding paragraph.

One simple estimate of minimum conductivity for a metallic number of carriers follows<sup>8</sup> from setting  $k_F = \pi/a$  and  $L = a$  in Eq. (1). This estimate, denoted here by  $\sigma_a$ , is given by

$$\sigma_a = \frac{e^2}{3\hbar a}. \quad (3)$$

A second lower limit on  $\sigma$  due to Friedel,<sup>11</sup> can be obtained by invoking the fact that the maximum scattering rate of conduction electrons by an impurity occurs when the magnitude of the phase shift induced by the scatterer is  $\frac{1}{2}\pi$ . This "unitarity limit" is closely approached for resonant scattering into a virtual bound state, and has been a useful concept in studies of the Kondo effect. It has also been applied to discuss the resistivity of concentrated rare-earth compounds. The unitarity limit on the conduction-electron lifetime is given by<sup>12,13</sup>

$$\frac{1}{\tau} \leq \frac{1}{\tau_u} = \frac{4(2l+1)}{\pi\hbar N_c(0)} \left( \frac{c}{V} \right), \quad (4)$$

where  $l$  is the virtual-bound-state angular momentum,  $c$  is the impurity scatterer concentration, and  $V$  is the atomic volume.  $N_c(0)$  is the unperturbed density of conduction-electron states at the Fermi level in the absence of scattering. Using Eq. (2) and the relation  $m^* k_F = \pi^2 \hbar^2 N_c(0)$ , valid for parabolic bands,

this result implies a lower limit on  $L$  given by

$$\frac{1}{L_u} = \frac{\pi^2}{k_F^2} \frac{4(2l+1)}{\pi} \left( \frac{c}{V} \right), \quad (5)$$

and since  $1/L = \Omega(c/V)$ , the maximum scattering cross section<sup>13</sup>  $\Omega_u$  can be discerned from Eq. (5). It is interesting to note that  $L_u$  does not depend on  $m^*$ , owing to the circumstance that  $\tau_u$  is proportional to  $m^*$ , although it should not be forgotten that  $m^*$  here refers to the unperturbed conduction-electron states. Putting  $L_u$  into Eq. (1) and using expressions given above for  $S_F$  and  $n$  yields the unitarity limit expression given by Friedel<sup>11</sup> for the resistivity, which is

$$\rho_u = \sigma_u^{-1} = \frac{4\pi\hbar c(2l+1)}{e^2 k_F p}, \quad (6)$$

where  $p = nV$  is the number of conduction electrons per atom. It is of great interest to compare  $\sigma_u$  with  $\sigma_a$ , which means comparing  $L_u$  with the interatomic separation  $a$ . For a metallic number of carriers,  $k_F \sim \pi/a$  and so  $\Omega_u \sim a^2$ . Then Eq. (5) shows that in the extreme case where every unit cell has a scatterer, so that  $c/V \sim a^{-3}$ , one has  $L_u \sim a$ , implying that  $\sigma_u \sim \sigma_a$ , i.e., that the two limits coincide in this extreme case.

The conductivity in Eq. (6) is based on a scattering theory linear in  $c$ , and is therefore somewhat suspect for  $c \sim 1$ . Mott<sup>8</sup> has, in fact, obtained a lower estimate for the minimum conductivity, denoted by him as  $\sigma_{\min}$ , by evaluating the general Kubo-Greenwood conductivity formula for conditions corresponding to the onset of Anderson localization. Presumably the difference between  $\sigma_{\min}$  and  $\sigma_a \sim \sigma_u$  entails scattering nonlinear in  $c$ . The regime between  $\sigma_a$  and  $\sigma_{\min}$  is one of great disorder in which the Fermi surface is undefined, and for the present purpose of comparing to nearly perfect Fermi-liquid behavior,  $\sigma_u$  suffices.

The dense scatterer limit just described has been applied<sup>14</sup> successfully to explain the maximum value of resistivity observed at  $T = 37$  K in  $\text{CeAl}_3$ , in the model that the  $4f$  state at each Ce site acts as a resonant scatterer of conduction electrons. Applying the same picture to  $\text{SmB}_6$  then yields a concrete estimate of the maximum resistivity increase which could be attributed to either thermal or impurity scattering. Cubic  $\text{SmB}_6$  has one Sm per unit cell with a valence  $\sim 2.6$ , and the Sm atom density is  $1.42 \times 10^{22}/\text{cm}^3$ , leading to  $p = 0.6$ ,  $c = 0.4$ ,  $V = 7.06 \times 10^{-23} \text{ cm}^3$ , and  $k_F = 6.32 \times 10^7 \text{ cm}^{-1}$ . Because the intraatomic Coulomb interaction separates states of differing  $4f$  occupation,  $l$  is taken to be 0 rather than 3. Equations (2) and (4)–(6) then yield the following unitarity limit values:

$$\rho_u = 5.44 \times 10^{-4} \Omega \text{ cm},$$

$$\mu_u = 1.35 \text{ cm}^2/\text{V sec}, \quad L_u = 5.61 \text{ \AA},$$

$$\Omega_u = \pi(3.16)^2 \text{ \AA}^2, \quad \tau_u = 7.69 \times 10^{-16} \text{ sec},$$

where the free-electron mass, probably appropriate for the conduction electrons, has been used to compute  $\tau$ . As expected the geometrical quantities  $L_u$  and  $\Omega_u$  involve lengths of about the lattice constant  $a = 4.133 \text{ \AA}$ .

The room-temperature resistivity of  $\text{SmB}_6$  was measured to be  $290 \mu\Omega \text{ cm}$ , not much less than the value of  $\rho_u$ . As the temperature is lowered,  $\rho$  increases to values well above  $\rho_u$ . In fact, the experimental low-temperature resistivity of  $2.6 \Omega \text{ cm}$  is about 5000 times larger than the value of  $\rho_u$ . For this resistivity, assuming a metallic number of carriers  $p/V = 8.5 \times 10^{21}/\text{cm}^3$ , and a free-electron mass to compute  $\tau$ , one finds

$$\mu = 2.79 \times 10^{-4} \text{ cm}^2/\text{V sec}, \quad L = 2.80 \times 10^{-4} a,$$

$$\Omega = \pi(53a)^2, \quad \tau = 1.59 \times 10^{-19} \text{ sec}.$$

Especially the geometrical quantities  $L$  and  $\Omega$  show how physically untenable is a scattering model for the resistivity rise if there is a metallic number of carriers. The conclusion from this comparison 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, i.e., hopping conduction.

Kasuya<sup>15</sup> has considered a model involving hopping conduction, in which perfect  $\text{SmB}_6$  would be a metal, but that disorder due to small numbers of Sm vacancies causes the states at the Fermi level to be Anderson localized. The very low-temperature conductivity was ascribed to hopping and the activation energy was then associated with excitation of carriers to delocalized states. This model is inconsistent with two experimental results. This first<sup>2</sup> is that the low-temperature conductivity increases, rather than decreases, with increased numbers of vacancies.<sup>4</sup> The second, pointed out by Kasuya,<sup>16</sup> is that the conductivity does not fall to zero as  $T \rightarrow 0$ , but saturates at the small value of  $0.38 (\Omega \text{ cm})^{-1}$ . He and his collaborators have measured the conductivity for temperatures down to 15 mK and found no decrease. Assuming that this behavior 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.

Section III B uses the Hall-effect data to estimate carrier concentrations and Sec. III C returns to the question of the size of the low-temperature conductivity.

### B. Estimate of the carrier concentration

In the absence of a detailed model for the electronic structure of  $\text{SmB}_6$  it is not possible to make a detailed analysis of the Hall effect, and especially its temperature dependence. But one basic idea which

can be employed is that the order of magnitude of  $R_H$  is determined by the number of carriers in the limit of collision-dominated transport. To proceed in this manner requires excluding from consideration situations in which the ratio of Hall mobility to the drift mobility differs greatly from one. Such situations are known, notably hopping conduction or the presence of magnetic moments which produce an anomalous Hall effect. A large anomalous Hall effect seems unlikely for  $\text{SmB}_6$  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 conduction have been set forth above.

The reason why small numbers of carriers cause a large  $R_H$  can be readily recalled from the simple classical picture of the Hall effect in which the force  $qE$  due to the Hall field  $E$  balances the force  $qv_d B$  due to the magnetic field acting on carriers with drift velocity  $v_d = J/nq$ , where  $J$  is the current density.  $R_H$  is defined as the field  $E$  for unit  $B$  and unit  $J$ . For unit  $B$ , a large  $E$  requires a large  $v_d$ , and for unit  $J$ , large  $v_d$  occurs only if  $n$  is small. The drift velocity is relevant if the carriers are scattered many times during their precession period in the magnetic field.

This condition requires  $(eB/m^*)\tau \ll 1$ ,

or  $\mu B \ll 1$ , which defines the low-field, collision-dominated regime. Since  $B = 10$  kG corresponds to  $B = 10^{-4}$  V sec/cm<sup>2</sup>, it is clear that the experiments described here were conducted in the low-field regime. The simple interplay of the magnitude of  $R_H$  and the value of  $n$  is not expected to be dramatically altered in more sophisticated treatments of the transport.

Even allowing for the presence of both holes and electrons leaves the conclusion unaltered. Consider the familiar model<sup>17</sup> of a hole band and an electron band, each with a spherical Fermi surface, characterized by electron and hole densities and mobilities,  $N_e, N_h, \mu_e, \mu_h$ , respectively. This is the simplest possible model for a system where  $R_H(T)$  has a zero crossing. Evidently, the two experimental quantities  $\rho$  and  $R_H$  do not completely determine the four model parameters. A straightforward analysis summarized in the Appendix yields the following conclusions for the case that  $R_H$  is negative (analogous results obtain with holes and electrons reversed for  $R_H$  positive). The one-band density  $(-1/R_H e)$  is an upper bound on  $N_e$ , with the two being equal if  $N_h = 0$ . For  $N_e < -1/R_H e$ ,  $N_h$  has a maximum value which depends on  $\beta = \mu_h/\mu_e$ , and at the conditions for maximum  $N_h$ ,

$$N_h \approx (-1/R_H e)/4\beta, \quad (7a)$$

$$N_e \approx (-1/R_H e)/4, \quad (7b)$$

$$\mu_h \approx 2\beta(-R_H/\rho), \quad (7c)$$

$$\mu_e \approx 2(-R_H/\rho). \quad (7d)$$

These simple results are here applied to the low-temperature values of  $R_H$  and  $\rho$  in  $\text{SmB}_6$  only to obtain order-of-magnitude bounds on the carrier densities. At 4 K,  $-1/R_H e = 2.08 \times 10^{17}/\text{cm}^3$  which is an upper bound on  $N_e$ . An upper bound on  $N_h$  entails a choice of a minimum value of  $\beta$ , which is obtained by choosing a minimum value of  $\mu$ . The physical content of the situation is that any number of holes can be present if their mobility is low enough to prevent them from dominating the Hall effect. For small numbers of carriers the minimum mobility implied by  $k_F L > \pi$  is rather large, but to obtain a maximal estimate of  $N_h$ , the minimum  $\mu$  will be taken as the metallic value  $\mu_u = 1.35$  cm<sup>2</sup>/V sec, determined in Sec III A. Since  $-R_H/\rho = 20$  cm<sup>2</sup>/V sec at 4 K in  $\text{SmB}_6$ , Eq. (7c) implies  $\beta \geq 0.1$  so that Eq. (7a) implies

$$N_h \leq 2.5(-1/R_H e) = 5.2 \times 10^{17}/\text{cm}^3.$$

This analysis then implies that the mobilities lie in the range 2 to 40 cm<sup>2</sup>/V sec.

The room-temperature values of  $R_H$  and  $\rho$  are, respectively,  $2.57 \times 10^{-4}$  cm<sup>3</sup>/C and  $290\mu\Omega$  cm. These can also be analyzed in the two-band model, using the relations of the Appendix but with hole and electron labels interchanged in defining  $\alpha, \beta$ , and  $\gamma$  because  $R_H$  is positive. The experimental one-band carrier density and mobility are  $1/R_H e = 2.43 \times 10^{22}/\text{cm}^3$  and  $R_H/\rho = 0.886$  cm<sup>2</sup>/V sec. The small value of  $R_H/\rho$  suggest  $\beta \sim 1$  so that neither  $\mu_e$  nor  $\mu_h$  will be too small. Equation (A5) shows that maximum  $N_e$  occurs for  $\gamma = 0.375$ , for which  $\alpha\gamma = 0.125$ , leading to  $N_e = 3.04 \times 10^{21}/\text{cm}^3$ ,  $N_h = 9.11 \times 10^{21}/\text{cm}^3$  and  $\mu_e = \mu_h = 1.77$  cm<sup>2</sup>/V sec. These upper-limit carrier densities are close to the average density of  $\text{Sm}^{3+}$  sites, the mobilities are close to the lower limits discussed above, and  $\rho$  is about half the unitarity-limit value.

These results imply that  $\text{SmB}_6$  at room temperature is a poor metal with  $\sim 9 \times 10^{21}/\text{cm}^3$  carriers being strongly scattered, and that the number of carriers decreases upon cooling to  $\sim 5 \times 10^{17}/\text{cm}^3$  at 4 K, causing the large conductivity decrease. Such behavior is realized by a small gap semiconductor model, and several have been proposed in the past for  $\text{SmB}_6$ .<sup>5, 18-20</sup> In the temperature range 4-13 K, the plots of  $\log_{10}|R_H|$  and  $\log_{10}\rho$  vs  $1/T$  are roughly linear, implying activation energies of 1.8 and 2.7 meV, respectively, and for the same temperature range Menth *et al.*<sup>16</sup> deduced an activation energy of 2.3 meV from their resistance data. A gap of the order of magnitude of these activation energies would be consistent with the bad metal picture<sup>2</sup> at room temperature where  $kT$  is about 10 times larger than the activation energy.<sup>20</sup>

### C. Low-temperature conductivity

The size of the low-temperature conductivity is an important issue. As mentioned above, the saturation of the conductivity fall as  $T \rightarrow 0$  implies that nonlocalized states exist at the Fermi energy. Further, since the conductivity at  $T=0$  is not infinite these states entail static disorder. Kasuya<sup>16</sup> has emphasized that the model for the ground state of perfect  $\text{SmB}_6$  must be consistent with the observed effects of static disorder. Citing an estimate of  $\sigma_{\min}$  of  $\sim 10^4 (\Omega \text{ cm})^{-1}$ , which is much greater than the observed conductivity, he argues that a novel model of the ground state is required to evade this conflict. To this end, he has proposed that the ground state of  $\text{SmB}_6$  is a Wigner lattice which, in the absence of disorder, would have an infinite conductivity at  $T=0$  due to phase slippage. Disorder pins the Wigner lattice and reduces the conductivity to the observed value.

Kasuya's model is innovative and interesting, but may not be necessary. The estimate of  $\sigma_{\min} \sim 10^4 (\Omega \text{ cm})^{-1}$  is somewhat larger even than the  $\sigma_a$  obtained above for a metallic number of carriers and  $L \sim a$ . A much smaller value can reasonably be estimated by taking account of the small low-temperature carrier density. In a narrow gap model defects such as Sm vacancies could shift the Fermi energy away from the gap center and produce band tails extending into, and possibly across the gap. For such a case, Mott<sup>8</sup> has given for  $\sigma_{\min}$  the expression

$$\sigma_{\min} = 0.026 \frac{e^2}{\hbar a_E} \quad (8)$$

where  $a_E$  is the distance between defects. An estimate of  $a_E$  is obtained here from

$$\frac{a_E}{a} = \left( \frac{n}{n_i} \right)^{1/3} \quad (9)$$

where  $a$  is the lattice constant,  $n$  is the metallic number of carriers,  $p/V = 8.5 \times 10^{21}/\text{cm}^3$ , and  $n_i$  is the low-temperature carrier density deduced from the Hall effect,  $\sim 5 \times 10^{17}/\text{cm}^3$ . Equation (9) yields  $a_E = 106 \text{ \AA}$ , for which  $\sigma_{\min} = 5.7 (\Omega \text{ cm})^{-1}$ . The reduced value of  $\sigma_{\min}$  compared to  $\sigma_a$  is due to two factors; the reduction in the number of carriers so that  $a_E > a$ , and the size of the coefficient 0.026 in Eq. (8) compared to  $\frac{1}{3}$  in Eq. (3), which is probably due to nonlinear scattering processes as mentioned at the close of Sec. III A. This estimate of  $\sigma_{\min}$  is 15 times, rather than  $10^4$  times, the observed conductivity. Given the general lack of detailed knowledge of the bands in a mixed-valent material, and of the effect of disorder upon them, as well as the difficulty<sup>8</sup> of assessing  $\sigma_{\min}$ , it is by no means obvious that a factor of 15 is cause for alarm. Finally, the experi-

mental fact<sup>4</sup> that the observed conductivity increases with degraded stoichiometry mitigates generally against any models in which defects reduce otherwise infinite conductivity.

### D. Conclusions

The low-temperature resistance rise in  $\text{SmB}_6$  has prompted several small-gap insulator models for this material.<sup>5,18-20</sup> However, various arguments for perfect-crystal metallic ground-state models have also been cited<sup>3,4,21</sup> and the existence of homogeneously mixed-valent insulators is not generally conceded. The most prevalent general model for the mixed-valent ground state is presently the two-component Fermi liquid,<sup>3</sup> although the possibility that  $\text{SmB}_6$  and some other mixed-valent compounds are not metallic has been raised again recently.<sup>2</sup> As analyzed above, resistivity and Hall-effect data strongly support a model in which the carrier density decreases from a metallic number  $\sim 9 \times 10^{21}/\text{cm}^3$  at room temperature to  $\sim 5 \times 10^{17}/\text{cm}^3$  at 4 K. The origin of the residual low-temperature conductivity could be band tail conduction, but is an important problem<sup>16</sup> which deserves further study.

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### APPENDIX

For the two-band model in the low-field regime,<sup>15</sup>

$$\rho = e (\mu_e N_e + \mu_h N_h)^{-1} \quad (A1)$$

and

$$eR_H = \frac{N_h \mu_h^2 - N_e \mu_e^2}{(N_h \mu_h + N_e \mu_e)^2} \quad (A2)$$

Equation (A2) readily takes the form

$$\gamma = \frac{N_e}{-1/R_H e} = \frac{1 - \alpha\beta^2}{(1 + \alpha\beta)^2} \quad (A3)$$

where  $\alpha = N_h/N_e$  and  $\beta = \mu_h/\mu_e$ . For  $R_H$  negative,  $\gamma$  is positive, and so it must be true that  $\alpha\beta^2 < 1$ . Therefore the value of  $\gamma$  is between 0 and 1, and achieves 1 for  $\alpha=0$ , implying that

$$N_e \leq -1/R_H e, \text{ for } R_H < 0 \quad (A4)$$

(A similar result holds for  $N_h$  when  $R_H > 0$ .) There is also a limit on the number of carriers of opposite sign, but it depends on  $\beta$ . Equation (A3) can be solved for  $\alpha\gamma = N_h/(-1/R_{He})$ , giving

$$\alpha\gamma = \frac{-(2\gamma + \beta) + (4\gamma + 4\gamma\beta + \beta^2)^{1/2}}{2\beta} \quad (\text{A5})$$

and the derivative of Eq. (A5) with respect to  $\gamma$  is

zero for

$$\gamma^* = \frac{1+2\beta}{4(1+\beta)}, \quad (\text{A6})$$

which is the condition for maximum  $N_h$ , as shown by the second derivative. For  $\beta < 0.25$ , which turns out to be the condition for  $N_h > -1/R_{He}$  (i.e.,  $\alpha\gamma > 1$ ),  $\gamma^* \approx 0.25$ . This leads to  $(\alpha\gamma)^* = 1/4\beta$ , or  $(\alpha\beta)^* = 1$ , and using Eq. (A1) one finds, for maximum  $N_h$ , the results given in Eq. (7) in the text.

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