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Studies of the correlated electron system SmB۶


1. Introduction

The heavy-fermion materials have properties that are now reasonably well established [1]. The quality of samples of these materials has never been a major issue because the dominance of the heavy electrons over most properties meant that defects and second phases tended not to be noticed. For UPt۳, issues of sample preparation and quality did arise and cloud the symmetry of the superconducting states and the temperature dependence of many properties [2], but in general this has not been a problem. Lately, it has been recognized that a few compounds with "semiconductor-like" ground states should be included in the highly correlated electron materials because the source of the energy gaps at low temperature is not clear and is probably caused by correlation effects [1].

Because a semiconductor-like gap is affected by anything that breaks the translational invariance of the lattice, it seemed useful to improve samples of one of these materials to see if different physics might be revealed. The compound SmB۶ has been studied by condensed-matter physicists for over 25 years and was recognized early as a compound with mixed valence on the samarium atoms [3]. The problem is to distinguish between intrinsic and extrinsic behaviors causing the energy gap. A particular aspect of SmB۶ is that it cannot even have a gap near a half-filled energy band because if the samarium were divalent, the material would be an insulator, and if it were trivalent, it would be half-filled. The samarium is clearly in between these valences, barely having a Fermi sea. Because single crystals of SmB۶ can be prepared in an aluminum solution, there is enormous variation possible in crystal growth conditions, and better crystals could be made. We made many growths of SmB۶, studied crystals by various techniques, and made some preliminary high-magnetic field measurements of resistivity. Most of the measurements were resistive because this tends to make interpretation of the data from a semiconductor view obvious. We simply went looking all around sample and measurement phase space with a Monte Carlo-like approach to see what could be found. We are beginning...
more systematic studies of our samples now because we
know what to look for and where. We report here on our
preliminary results.

2. Experiments

We prepared 26 useful batches of crystals of SmB$_6$
by precipitation in molten aluminum. Weighed amounts of
samarium, boron, and aluminum were placed in an
alumina crucible and heated slowly to 1500°C in a he-
ilium atmosphere. Various cooling ramps of up to 200 h
were used to cool the solution to the melting point of
aluminum 670°C. The crystals were extracted by dissolv-
ing the aluminum from them in a warm, concentrated
NaOH solution. To optimize the sample quality, in these
preparations the Sm to B atomic ratio was varied from
1:4 to 1:8, and the atomic ratio of Sm to Al was varied
from 1:17 to 1:393. The purities of the elements used late
in the study were Sm – 99.99%, B – 99.5%, and Al
– 99.999% to minimize cost while improving samples.
The crystals could be etched with dilute HNO$_3$. We
performed modest representative studies of the crystals
with X-ray diffraction, with scanning and transmission
electron microscopy, and with optical microscopy. Res-
istance measurements were with four leads and were
made with many techniques both AC and DC. Magnetiz-
ation measurements were made with a Quantum Design
Squid System.

3. Results

The quality of SmB$_6$ samples has been judged by the
resistivity increase from room temperature to liquid-he-
ilium temperature, called here the resistivity ratio RR [4].
This is certainly a reasonable approach to screening
many samples to select the ones with the cleanest energy
gaps and is distinct from metals for which the resistivity
decreases when cooled. We found that a modest etch of
the samples to remove 10-30%/o of their weight could
raise the RR by a factor of at least two up to almost
a factor of five. Hereafter all of the results discussed come
from etched samples. However, what is more important
here is that this result shows that the surface of the single
crystals is a conductor that is not representative of SmB$_6$.
What-is-etched-off is shorting out the intrinsic resistance
of SmB$_6$ and causes the resistance to begin to saturate
near a temperature of 4 K because its resistance is far
below that of pure SmB$_6$ below 4 K. The removed mater-
ial has the resistive behavior of a dirty metal; that is, it is
temperature independent at low temperature. We were
led by this result to fit the resistance of the samples at low
temperature to a parallel-resistor model. We took the
sample to be composed of a constant resistance $R_A$ in
parallel with a resistance expressed by $R_{Be}^{1/2}$ and show
one fit in Fig. 1. Our fits are all very good. For this fit,
$R_A$ is 102 $\Omega$, $R_B$ is 0.034 $\Omega$, and $A$ is 48.1 K. For this
sample, the resistance above about 4 K is thus dominated
by the energy gap and shows an exponential behavior,
whereas, below about 4 K, the constant series resistance
from surface crud dominates the resistance. This is why
all reported data show this sort of saturation somewhere
near 4 K followed by only a very weak increase in resist-
ance at lower temperatures. We realize that this result
modifies the interpretation of previous data taken below
4 K, but this parallel-resistor picture reflects what hap-
pens upon surface etching and is more than heuristic.
Because the crystal surface is in contact with the alumi-
umn solvent as the aluminum solidifies and cools to
room temperature, with different contraction than SmB$_6$,
it is simple to imagine that we do not want to study this
surface. This could easily mess up an energy gap of the
surface of a material. Our results suggest that the more
we etch, the better the sample gets (more activated); so
that the surface crud is not a discrete layer but rather is
continuously changing spatially.

Because some variation in the RR can be due to
extrinsic states in the energy gap, we show in Fig. 2 that,
within our scatter, there is no variation of the gap with
RR over a large range, as is the case for semiconductors.
We have some evidence that the gap does vary as a func-
tion of the samarium to boron ratio, which is taken as
1:6 but has a huge variation possible [5]. Our prelimi-
nary results (not shown) have a maximum gap energy of
80 K at exactly the ideal ratio to within 0.1 at% vari-
ation. The best samples clearly come from batches with
the highest ratio of aluminum, that is, very dilute SmB$_6$. 
Fig. 2. The energy gap of various samples as a function of the increase in resistance from room temperature to 4 K for each sample.

Fig. 3. The resistance of a typical sample plotted to emphasize the maximum near a temperature of 150 K.

Our transmission electron microscopy on ground samples of SmB₆ shows regions of SmB₄ within the samples and occasional edge dislocations within the SmB₆. Our scanning electron microscopy shows many types of defects on the surfaces. Our best samples are relatively free of these, but inclusion of aluminum, edges notched like a comb, and tetrahedral pyramids with their bases parallel to the edges of the crystals all do show up. Our magnetic susceptibility measurements confirm what has been reported for many years [3]. We do notice that bad samples have a distinct and large 1/T tail at low temperatures, while better samples show only a monatomic decrease in susceptibility down to our lowest temperature of 5 K. Clearly, samarium that is not at the proper crystallographic sites can be seen magnetically in low-temperature tails. Further work is underway on this measure of sample quality.

Fig. 3 shows a resistance curve plotted to emphasize the maximum near 150 K. Only Lacerda et al. have reported this before [6]. We see it in all of our better samples, and it might be associated with the "unconventional" magnetic excitation at 13–14 meV seen by neutron scattering [7]. The magnetoresistance of SmB₆ at 40 mK up to a field of 50 T is shown in Fig. 4. To the best of our knowledge, this field and temperature range has not been used before for any published results. Note that the parabolic negative magnetoresistance turns around between 20 and 30 T showing the beginning of saturation. The magnitude of the magnetoresistance is far less than the negative 40% reported at 4 K for the same field range [6]. Our preliminary result at 4 K shows an even larger value at 4 K for the sample used in Fig. 4. Either, the magnetoresistance is indeed decreasing significantly at lower temperatures, which is most unusual, or the data below 4 K are simply measuring the parallel, dirty resistance instead of the SmB₆ behavior, which is seen at 4 K and above, as already discussed.

4. Conclusions

Better samples of SmB₆ have been prepared and measured. The results hold some surprises because the resistive saturation at low temperature is a dirt effect and the activated behavior may hold to the lowest temperature. We note that the resistance maximum near 150 K highlights that this material is not simply a semiconductor at all temperatures. The gap only appears well below room temperature. Some earlier work should be redone with
better samples in order to help understand the cause and properties of the low-temperature, energy gap in SmB$_6$.

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