picture of the moon's surface. It is equivalent to a crater 20 m in diameter and 6 m deep which, according to the Ranger photographs, should occur on the average with a frequency of one crater per 10 000 m^2.[4]

Since the energy partition ratio γ as well as τ depends on kz, a detailed analysis of the seismograph response with time as a function of frequency should give information about the distribution in depth of the principal obstacles and tell whether one is dealing with surface craters or heavy meteorites embedded at some depth. That roughness could have a bigger effect on surface waves on the moon than on the earth is of course not unreasonable: The absence of atmospheric weathering and the larger number of embedded meteorites would make the moon's surface much rougher on the scale of tens of meters.

An alternative explanation of the duration of seismic signals is that the original disturbances set off secondary events due to instabilities of the lunar surface. The trapping of surface-wave energy proposed by us would also tend to enhance the period during which secondary disturbances could occur. In that case, however, the spectral decay should depart significantly from Eq. (4).

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ELECTRONIC AND MAGNETIC STRUCTURE OF SmB6

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(Received 16 October 1969)

A new electronic configuration involving localized $6s$ electrons is hypothesized for the Sm ions in SmB$_6$. The model is successful in explaining earlier results of susceptibility measurements and new Mössbauer spectroscopy data reported here.

Recently, a number of reports[1-3] discussing the unusual electric and magnetic properties of SmB$_6$ have appeared. This paper presents new data, obtained by Mössbauer-effect measurements on Sm^{149}, which help establish the electronic structure of the Sm ions. The results of the Mössbauer experiments are combined with the previously published information to develop a new model which seems to explain the observed properties.

Briefly outlining the results reported in Ref. 1, the electrical characteristics of the material appear to be semiconducting, with resistance sharply increasing down to 3°K, and thereafter increasing only very slowly. The system does not order magnetically down to below 0.35°K, and the temperature dependence of the susceptibility is complex and not consistent with what would be expected from either Sm^{2+} or Sm^{3+} ions. The earlier work attributed the unusual behavior to a thermally excited electronic transition; the Sm ions were considered to be divalent at low temperature and trivalent at high temperature.

This electronic transition has been used as the basis for recent theoretical articles[2,3] discussing the temperature dependence of the conductivity. We present here a different analysis of the SmB$_6$ electronic structure.

The Mössbauer isomer shift measures the density of s electrons at the Sm nucleus. In rare-earth ions, a change in the number of $4f$ electrons results in a changed shielding of the s electrons (especially the two $5s$ electrons), so that an increase in the number of $4f$'s increases the shielding and decreases the net s density at the nucleus. This shielding effect is much larger than the direct change in s density obtained by a change in $6s$ configuration; thus the measured isomer shift provides a direct measurement of the number of $4f$ electrons. The results of our measurements of isomer shift as a function of temperature are shown in Fig. 1(a). Comparison of the results with those for Sm in known valence states shows that the Mössbauer line falls at neither the Sm^{2+} ($4f^6$) nor Sm^{3+} ($4f^5$) valence position, but in between. Since rare-earth ions,
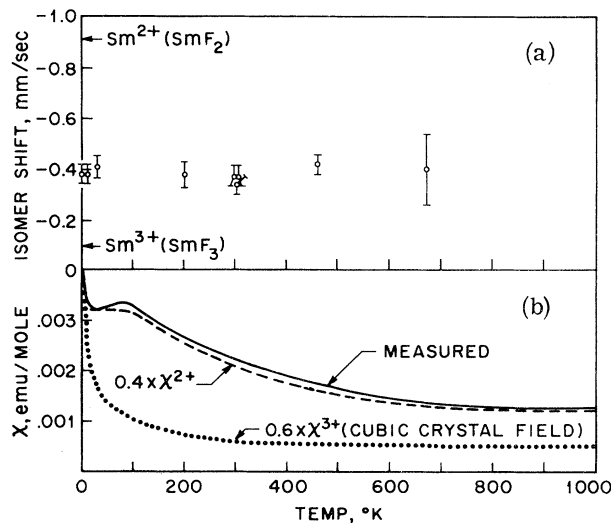
FIG. 1. (a) Isomer shift (corresponding to s-electron density at the Sm^{149} nucleus) versus temperature for SmB_6. Measurements made on a number of samples, including the one described in Ref. 1, were in agreement. Typical values measured for ionic Sm^{2+} and Sm^{3+} compounds are also shown. The data have not been corrected for second-order Doppler shift, which is temperature dependent. The high effective Debye temperature of the hexaboride materials should make this correction small below 400°K. (b) Measured and calculated susceptibilities, χ, of SmB_6. Solid line, data of Ref. 1, replotted. Dashed curve, 40% of the molar χ of Sm^{2+}, calculated using the Van Vleck model. Dotted curve, 60% of χ for the $4f^5$ configuration using the results of Ref. 4 with a cubic crystal-field splitting of $\Delta/k = 100$°K. It can be seen that the sum of the two theoretical contributions far exceeds the experimentally observed value at low temperatures. The small rise in the data below 10°K does not have $1/T$ dependence and is tentatively attributed to impurity effects by the authors of Ref. 1.

even in metals, appear to be essentially always identifiable as having an integral number of $4f$ electrons, it does not seem reasonable to explain this deviation by assuming that the ion has a nonintegral $4f$ configuration. The semiconducting properties of the material exclude large conduction-electron contributions to s density as a source of isomer shift.

The correct explanation for this anomalous isomer shift appears to be simultaneous presence of both $4f^5$ and $4f^6$ Sm ions in the SmB_6. Because the isomer-shift difference between the two electronic states is only about $\frac{1}{3}$ the observed linewidth, the two valence states would not be resolved as two separate peaks. A single peak in the Mössbauer spectrum, intermediate in po-

sition between those for divalent and trivalent Sm, is observed. Any conversion of divalent to trivalent ions would appear as a shift of the line toward the trivalent position. As can be seen in Fig. 1(a), no significant change occurs in the temperature range we have studied. The observed line is too broad to allow us to distinguish between the possible cases of rapid relaxation and slow relaxation between $4f^5$ and $4f^6$.

The picture we present here is fully in agreement with some previous work[5] on L-absorption spectroscopy of SmB_6 from 150 to 670°K. Those authors estimated that $35 \pm 5\%$ of the Sm ions were in the divalent state, and this estimate would result in the isomer shift we observe. Thus, the Mössbauer and x-ray measurements lead to a consistent picture in which a temperature-independent fraction of the Sm ions is divalent. This analysis is also supported by comparing the lattice constants of the divalent RE hexaborides (Eu and Yb) with those of the trivalent rare earths; again, SmB_6 is seen to lie between the RE^{3+} and RE^{2+} compounds, slightly closer to the 3^+ compounds.

To have an acceptable model, however, it is necessary to show that this analysis also produces the experimentally observed susceptibility. Figure 1(b) shows the data of Ref. 1. Divalent Sm ions are isoelectronic to Eu^{3+}, and show (at low temperatures) the well-known Van Vleck temperature-independent susceptibility, due to the second-order Zeeman mixing of the $J=0$ ground state with excited states of the $4f^6$ configuration. The susceptibility (χ^{2+}) is substantially independent of crystal-field effects and can be accurately calculated with only the (well known) L-S-coupling strength as a parameter.[6] Figure 1(b) shows that the susceptibility resulting from 40% of the Sm ions being divalent comes very close to that actually measured in SmB_6. However, the susceptibility for the 60% of Sm ions assumed to be 3^+ must be added to that of the divalent ions. The susceptibility of the Sm^{3+} in the cubic SmB_6 symmetry[7] can be calculated directly[4] with only the (cubic) crystal-field splitting Δ as a free parameter. Regardless of the value chosen for Δ, the behavior is dominated by the $1/T$ term resulting from the fact that the ground crystal-field state is a Kramers doublet. It can readily be seen that the addition of χ^{2+} and χ^{3+} produces a susceptibility that is far larger than the experimental result below ~100°K. In fact, no ratio of divalent to trivalent Sm ions can reproduce

the susceptibility observed at low temperatures. The likeliest explanation for this puzzle is that the Sm ions which do not have the $4f^6$ configuration have only a negligible magnetic moment, by virtue of the cancellation of the moment of the $4f^5$ configuration by a bound electron,[8] so that the Sm ions that are not $4f^6$ are $4f^5 5d^x 6s^y$. We can see from the existence of many metallic Sm compounds with $4f^5$ configuration that this configuration is a reasonable one energetically. In the metallic compounds, the hybridized extra electron becomes part of the conduction band. Apparently, in the SmB_6 lattice, the last electron finds it energetically perferable to stay localized on or near the Sm ion, rather than going into the conduction band as it does in the hexaborides of the trivalent rare earths. The result is superficially like the "Kondo state" formed by the condensation of conduction electrons on local moments in metals. To our knowledge, this is the first suggestion of localized $6s$ states in rare earths.

The moment of the $4f^5$ $(J = \frac{5}{2})$ configuration calculated using the cubic crystal field as above is $0.6 \mu_B$ at $2°K$ and rises to $1.6 \mu_B$ (by thermal population of the upper crystal-field state, which has a larger moment) at $100°K$. Thus, the spin moment alone of one bound electron is more than enough to compensate that resulting from the $4f$ electrons at low temperatures. It is tempting to say that there is 0.6 $6s$ electron providing exact cancelation of the low-temperature $4f$ moment (and not quite enough to cancel the $100°K$ $4f$ moment, explaining why the experimental points rise slightly above the divalent-susceptibility value in that region). However, the exchange energy of the hybridized electron with the $4f$'s is so large that the cubic crystal-field model used to calculate the $4f$ susceptibility is unrealistic in this case. The complex behavior produced by the combination of the crystal field and the exchange coupling from the $6s$ electron may well explain the minor differences between the observed χ and that from the $4f^6$ Sm ions. An exact analysis might show a mechanism[9] producing exact (i.e., nonaccidental) cancelation of the $4f$ moment by the localized electron as occurs in the Kondo case.

The size of the measured susceptibility establishes beyond a doubt that most of the Sm ions are not in the $4f^6$ configuration. The lack of a $1/T$ tail on χ at low temperatures and the failure to obtain magnetic ordering exclude the possibility that the remainder of the Sm is in the normal trivalent $4f^5$ configuration.

We have made further tests of this by looking for hyperfine structure in the Mössbauer spectrum of SmB_6 at temperatures down to $1.2°K$, a temperature at which all trivalent Sm compounds we have studied show either magnetic order or paramagnetic hfs. Neither of these effects was observed. Additionally, at $1.2°K$, a 12-kOe magnetic field was applied to the sample. Negligible broadening of the observed spectrum showed that under these conditions the field H_{int} at the Sm nucleus was less than 40 kOe. Since an H_{int} of approximately 200 kOe would be expected under these conditions from the $4f^5$ configuration in the cubic crystal field, this represents additional evidence that the Sm ions are in some sort of "nonmagnetic" state. Our analysis in terms of the $4f^5 5d^x 6s^y$ state appears to be likeliest from energetics and the known semiconducting character of SmB_6. If this complex state has a substantial unpaired $6s$ component, satisfactory agreement of our model with the Mössbauer spectra also requires that the $4f^5 5d^x 6s^y$ configuration is not constant in time, but that there is a continual jumping between this state and the $4f^6$ state. This relaxation rate must be fast (e.g., $\sim 10^{11}$ sec^{-1}), compared to the Larmor frequency of the Sm nucleus in the large field of the $6s$ electron, to destroy the hyperfine interaction due to the $6s$ contact term. This high relaxation rate is only likely if the "jumping" electron stays localized on the same ion.

The results presented here, insofar as they predict semiconducting behavior as is observed in hexaborides of other divalent metals, are consistent with the observed temperature dependence of the conductivity. We have not made a detailed analysis of the transport properties expected in this model. All the Sm ions are crystallographically equivalent, which would allow charge hopping from ion to ion as a conduction mechanism.

The constancy of the Sm^{149} isomer shift as a function of temperature suggests that SmB_6 is not a good example of the semiconductor-metal transition suggested recently by Falicov and Kimball,[2] since the hypothesized promotion of Sm $4f$ electrons into the conduction band should produce a substantial isomer shift, in contrast to what is observed.

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by E. Buehler.

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[8]The systematics of free-ion energy levels show that
the $4f^56s$ configuration lies 1 eV below the $4f^55d$ state.
In the crystal the greater overlap of the $6s$ wave func-
tion with the ligand charge distribution should remove
most of this difference. A realistic detailed model
should include hybridization of the $5d^x6s^y$ wave func-
tion with that of the electrons on the boron ions; i.e.,
$x+y\neq1$.

[9]For example, in the approximation of strong L-S
coupling within the $4f$ shell, moderate exchange be-
tween the $6s$ and $4f$ electrons, and weak crystal field,
the ground state of $4f^56s$ would be $J=2$, which has a
nonmagnetic Γ_3 state in the cubic crystal field.

MANY-BODY EFFECTS IN PHOTOEMISSION*

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A many-body formalism utilizing a tunneling operator is proposed for the photoemis-
sion process, thereby avoiding the artificial separation of the process into distinct steps.
The lowest-order term in the formalism, corresponding to surface scattering, is devel-
oped in detail for simple metals. Energy-distribution curves from this "surface term"
are presented for both free and interacting electrons. Many-body effects, including
plasmarons, are prominent in the latter and have tentative experimental support.

The standard model of photoemission repre-
sents the emission process as a sequence of
three steps wherein the electrons are first opti-
cally excited, then proceed to the surface, pos-
sibly scattering en route, and finally escape over
a surface barrier.[1] While the model has greatly
facilitated interpretation of data it is, nontheless,
phenomenological and does not include the possi-
bility of many-body interactions. Several au-
thors[2-4] have discussed the importance of such
interactions in the first step, the optical excita-
tion, although they have not departed essentially
from the three-step viewpoint. In contrast, the
model below incorporates many-body interaction
throughout the photoemission process, inseparab-
ly intertwining the three steps. It is, I believe,
the first model to treat the whole photoemission
process from a unified, many-body viewpoint
with results for interacting electrons.[5] In this
Letter the lowest-order term in the formalism,
corresponding to a surface-aided process, is de-
veloped.

Volume processes rather than surface process-
es are generally considered to be most signifi-
cant for photoemission in metals.[3,6,7] However,
it has become clear that the emitted-electron en-
ergy-distribution curves (EDC's) are very sensi-
tive to the condition of the surface and, further-
more, that electrons emitted when the incident-
photon energy is on the order of or greater than
the (volume) plasmon energy ω_p originate from a
very shallow mean depth, estimated to be less
than 20 Å in alkali metals[7,8] and nickel.[9] It thus
becomes interesting to investigate the lowest-or-
der, surface term in the model.

The basic Ansatz in the model is that the es-
cape of an electron from the metal into the vacu-
um can be mathematically represented by a tun-
neling operator, or transfer Hamiltonian, much
as is done in superconductor and semiconductor
tunneling.[10] Specifically, let H_m be the (exact)
Hamiltonian of a metal of infinite extent, and H_v
the Hamiltonian for free particles in a vacuum of
infinite extent. The respective eigenstates occu-
py separate Hilbert spaces. The emission of an
electron from the metal is represented as a per-
turbation on $H_0 \equiv H_m + H_v +$ (electromagnetic inter-
action with incident light) in the form

$$H = H_0 + T,$$

$$T = \sum_{k,k'} T(\vec{k}, \vec{k}')a_k{}'b_k{}^\dagger + \text{H.c.}, \qquad (1)$$