by the recent theories of Jaros and co-workers.[12] I shall consider possible origins of these effects and of the large two-electron binding energy in a later publication.

The most compelling of the many facts supporting this new interpretation are the anomalous phonon structure in the DH spectra and the agreement with the two-electron excitation spectra of Samuelson and Monemar.[10] On the other side one could cite the argument of Dean[9] and the similarities found by Carter *et al.*[13] between the excited-state energies observed by DH and those expected and observed for shallow donors in GaP. It is hoped that this Letter will stimulate the crucial experiments which will clarify the nature of this most peculiar deep center.

It is a pleasure to acknowledge many valuable discussions with L. Samuelson and with L. -Å. Ledebo, B. Monemar, and C. Ovren and to thank Professor H. G. Grimmeiss and the Department of Solid State Physics of the Lund Institute of Technology for their hospitality and support during my visit there, where a part of this work was performed. I am indebted to P. J. Dean for helpful critical comments. This work has been supported in part by the U. S. Air Force Office of Scientific Research under Contract No. F49620-77-C-0005.

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Evidence for Varying *d*-Band Occupancy across the Trivalent Rare-Earth Series

B. Delley, H. Beck, H. U. Künzi, and H.-J. Güntherodt
Institut für Physik, Universität Basel, Basel, Switzerland

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The resistivity of liquid Lu, which has been measured for the first time up to 1800°C, has a negative temperature coefficient. In the framework of structural-disorder scattering this means that $2k_F$, the diameter of the Fermi sphere of conduction electrons, lies close to the wave number K_p of the first peak of the structure factor. This is consistent with recent band-structure calculations by Duthie and Pettifor providing good evidence that the number of s electrons per atom changes from about 0.5 for La to 1.5 for Lu.

The purpose of this Letter is to bring together two ideas developed in different contexts in order to obtain new insight into the electronic structure and electronic transport properties of liquid rare-earth metals. This concept is confirmed by the measurement of the resistivity of liquid Lu to be reported below.

Firstly, the concept of scattering from structural disorder has been very successful in explaining the electrical resistivity ρ of liquid and amorphous metals. This field started with the study of the simple metals, for which an explanation of ρ is provided by the nearly-free-electron (NFE) theory proposed by Ziman.[1,2] The main success of this theory is the explanation of the negative temperature coefficient (NTC) of the so-called divalent simple metals such as Zn.[3] For those metals $2k_F$, the diameter of the Fermi sphere, is very close to K_p, the wave number of the first peak of the structure factor $S(q)$. It is the variation of $S(q)$ with temperature which determines the temperature dependence of ρ. As the temperature is increased, the height of this peak is reduced and therefore ρ can decrease.

The occurrence of NTC in liquid systems such as divalent metals Ba,[4,5] Eu,[5] Yb,[5] and alloys of monovalent noble,[3] transition[3] (T), and rare-earth (RE) metals[5] with polyvalent metals has led to a very successful extension of this simple liquid-metal theory to T and RE metals and their alloys. For these metals, the simple NFE arguments become more suspect since the resistivities are large and the mean free path can be of the order of only twice the interatomic distance. Furthermore, in the T and RE metals, there is the possibility of spin-disorder scattering contributing to ρ.

For T and RE metals, the electron-ion interaction is represented by a suitable muffin-tin potential, replacing the pseudopotential used for simple metals. In the single-site t-matrix approximation of multiple-scattering theory, one then obtains the electrical resistivity[6]

$$\rho = \frac{3\pi\Omega_0}{4e^2\hbar v_F^2 k_F^4} \int_0^{2k_F} dq\, q^3 |t(q, E_F)|^2 S(q), \qquad (1)$$

where Ω_0 is the atomic volume. Magnitude and temperature dependence of ρ are governed by two facts: (1) The phase shifts $\delta_l(E)$ of the atomic potential determine the single-site t-matrix $t(q, E_F)$ at the Fermi energy E_F. (2) As stated above for simple metals, the size of $2k_F$, relative to K_p, has a decisive influence on the temperature dependence of ρ. The resistivity values of many T metals and the temperature dependence—especially the NTC occurring for alloys of T metals and polyvalent metals in some concentration ranges—calculated along this line[6] agree quite well with experiment under the assumption that k_F corresponds to a number n_s of conduction electrons of somewhat less than one per ion.

Experimental values for ρ through the liquid RE series are comparable to those of liquid T metals. Except for the divalent elements Eu and Yb, ρ increases monotonically from La to Lu (see Fig. 1). Here, we have included the new results which we report for Lu in this Letter.

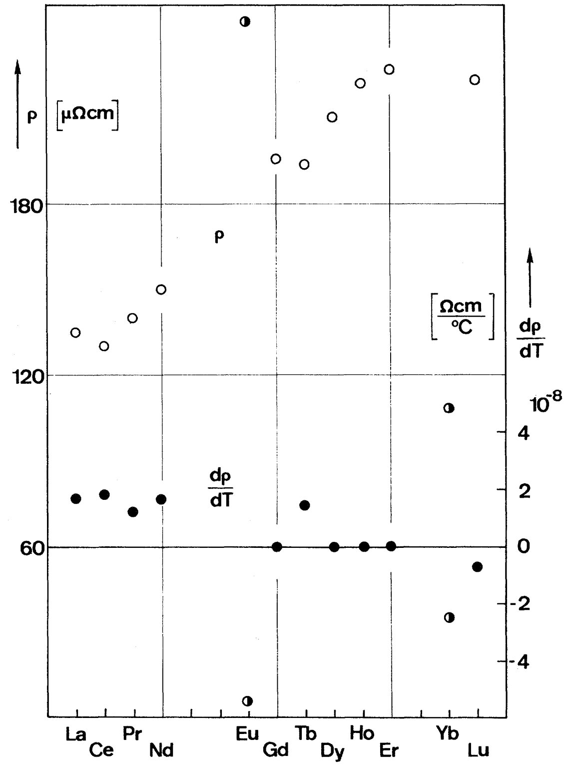

FIG. 1. Electrical resistivity and its temperature derivative for the liquid rare-earth series.

The electrical resistivity of Lu has been measured from room temperature up to 1800°C. The experiment is very exciting by itself. To our knowledge, it is the first measurement of ρ for any liquid metal under steady-state conditions up to such high temperatures. The resistivity measurements were performed using the four-point probe method with an ac current of 310 Hz in a vacuum of 10^{-6} Torr. Lu of 99.9% purity were contained in thin-walled crucibles made out of the refractory metal Ta. The resistivity of liquid Lu was determined by assuming that the resistance of the measuring cell is parallel to the resistance of the liquid-metal sample. The empty Ta container has been measured over the entire temperature range. The thermal expansion of the Ta cell gives a small contribution, which has been taken into account. A number of cross checks with other liquid metals were made in order to test the reproducibility of the resistivity measurements. We estimate our error in measuring the absolute resistivity to be ±3% and in measuring resistivity ratios better than ±0.1%.

Figure 2 shows ρ as a function of temperature for Lu. In the solid state, ρ shows an extremely

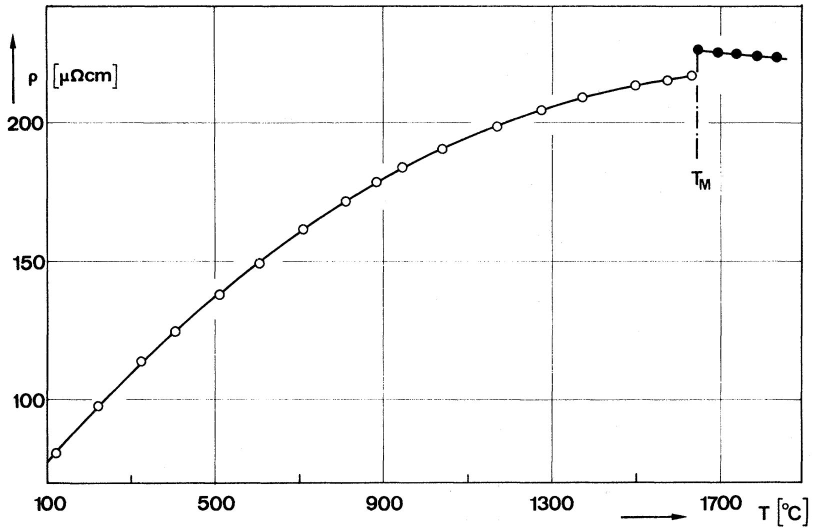

FIG. 2. Resistivity of Lu as a function of temperature.

nonlinear temperature dependence, which is very interesting in its own right. Above the melting point, ρ decreases with increasing temperatures. This is characteristic of the liquid divalent metals Zn,[3] Ba,[4,5] Eu,[5] and Yb,[5] showing NTC, but it is rather surprising for the trivalent element Lu.

In order to compute ρ for the Re metals by means of Eq. (1) we have constructed muffin-tin potentials for La, Gd, and Lu. The phase shifts show the following qualitative behavior (details will be published elsewhere): the d shift δ_2 is dominant, showing a resonance-type behavior as for the T metals, although the s phase shift δ_0 is also quite large in the energy range of interest. With increasing atomic number (i.e., from La to Lu) the d resonance energy shifts to higher values. Calculations for the crystalline phase[7] as well as our preliminary estimates for the liquid show that the Fermi energy moves in the same direction; therefore the phase shifts will be more or less constant throughout the trivalent RE series. Thus we expect the increase of ρ between La and Lu to be due to an increase in $2k_F$ via the contribution from $S(q)$.

Secondly, a recent Letter by Duthie and Pettifor[8] has shed some light on this problem. They performed self-consistent band-structure calculations for various (crystalline) RE elements in order to explain the sequence of crystal structures occurring under pressure. From the relative position of the bottoms of the s and d bands, as well as the Fermi energy, they were able to determine the fractions n_s and n_d of the three valence electrons, which are in s-like and d-like states, respectively. They find an increase of n_s through the RE series: For La $n_s \simeq 0.5$ and $n_d \simeq 2.5$, whereas for Lu $n_s \simeq 1.1$ and $n_d \simeq 1.9$. Accounting for s-p hybridization[8] may change the numbers for Lu into $n_s \simeq 1.5$ and $n_d \simeq 1.5$. These results are consistent with older band-structure calculations[7] which show that the energy region covered by d bands for Lu is broader than for La and that it lies higher above the bottom of the conduction band.

It seems reasonable to assume that the numbers n_s and n_d will be about the same for the liquid as for the crystalline state. If the electrical transport in trivalent RE metals is predominantly due to s electrons, then $2k_F$, entering Eq. (1), will be the diameter of a Fermi sphere containing n_s electrons per ion. Therefore $2k_F$ will be largest for Lu, which yields the increase of ρ through the Lanthanide series discussed above. This is also in agreement with the behavior of the temperature coefficient across the RE series. For the light RE metals the temperature coefficient of ρ is positive, whereas for the heavy RE metals within the experimental error this quantity decreases to zero and becomes even slightly negative for Lu.

We expect that, for liquid Lu, $2k_F$ is very close to K_p. Since neither Ω_0 nor $S(q)$ are measured for liquid Lu we make the following estimate: Ω_0 is calculated from the known value of La by assuming the same density ratio α between La and Lu as in the solid. Taking a value of $n_s = 1.3$ for Lu (lying between the limits of 1.5 and 1.1 of Ref. 8) yields $2k_F \simeq 2.1$ Å^{-1} for free electrons.

Scaling the K_p value of La[9] by $\alpha^{1/3}$ we obtain $K_p \simeq 2.2$ Å^{-1} for Lu. We are thus able to explain this NTC observed for the first time in a trivalent pure liquid RE by applying the following two ideas: (1) the concept of scattering from structural disorder and (2) the increase of $2k_F$ values across the trivalent RE series.

From a theoretical point of view it would, of course, be desirable to calculate partial densities of states directly for the liquid. Reliable calculations for liquid RE metals with strong electron-ion interaction are, however, very difficult. Our results show that the simple picture of a Fermi sphere containing n_s conduction electrons per atom is very useful for interpreting the transport data in the liquid state. Moreover, as the example of Lu shows, the experimental data for ρ and $d\rho/dT$ can be used to estimate the magnitude of $2k_F$ and thus the numbers n_s and n_d in this simple model. In contrast to the divalent liquid metals Eu and Yb which already have roughly two conduction electrons per atom, corresponding to a $2k_F$ value close to K_p, liquid trivalent Lu has the required $2k_F$ value only as a consequence of the varying number of d and s electrons across the RE series.

The T dependence of ρ for a liquid metal when alloyed with elements of known valence can also be used to get information about $2k_F$. Therefore we have measured ρ for RE alloys such as La-Sn, Gd-Sn, and Ce-In (see Fig. 3). All three liquid alloys are characterized by showing NTC. This can only mean the following: Alloying a RE, having $2k_F < K_p$, with a polyvalent metal increases the electron density and $2k_F$ increases so that this quantity coincides with K_p, the position of the first maximum in the partial structure factors.[10] This leads to enhanced structural-disorder scattering and hence to a maximum in ρ and the possibility of NTC at certain alloy concentrations. These concentration ranges showing NTC are very strongly related to the $2k_F$ values of La, Gd, In, and Sn. The assumption that $2k_F$ for La is smaller than for Gd is reflected in the experimentally observed fact that the NTC in Gd-Sn alloys occur at lower Sn concentrations than in La-Sn alloys. The difference in the $2k_F$ values of In and Sn is nicely seen in the occurrence of NTC in Ce-In at higher concentrations of the polyvalent metal than in La-Sn. On the other hand, alloying two trivalent rare-earth metals should only lead to weak concentration dependence of ρ and no NTC since $2k_F$ never passes through the peaks in the partial structure factors. The resistivity of La-Gd alloys indeed seems to behave in this fashion.[5]

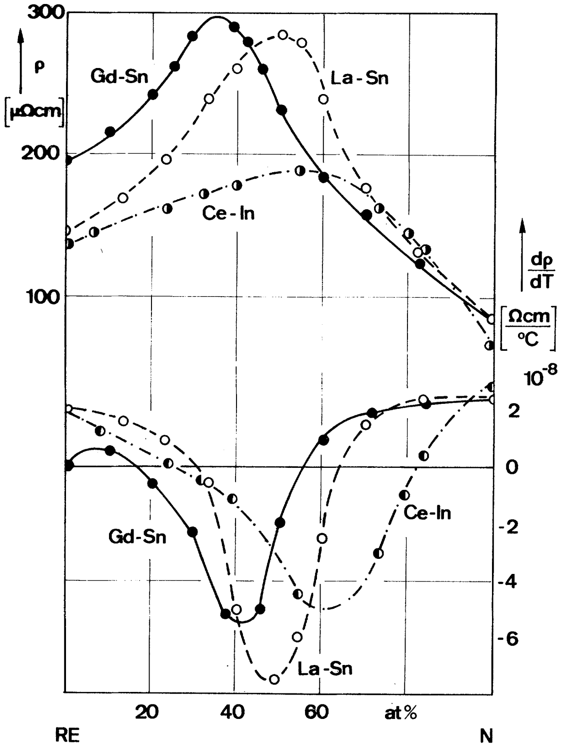

FIG. 3. Resistivity and temperature coefficient for the liquid alloys La-Sn, Gd-Sn, and Ce-In.

In summary, we have shown that the temperature coefficient of ρ changes through the Lanthanide series from being positive for liquid La to being slightly negative for Lu. In the framework of Ziman's theory, this can be explained by an increasing value of $2k_F$. This is consistent with a number of s electrons increasing from $n_s = 0.5$ to as much as $n_s = 1.5$ for Lu. The temperature coefficients for various alloys also fit well into this scheme.

We are indebted to Dr. R. Evans for many helpful discussions and to Professor B. Johansson for drawing our attention to Ref. 8. Financial support of the Swiss National Science Foundation is gratefully acknowledged.

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Observation of the Band-Hopping Transition for Electrons in Naphthalene

L. B. Schein and C. B. Duke
Xerox Corporation W114, Rochester, New York 14644

and

A. R. McGhie
Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 26 October 1977)

Transient photoconductivity has been used to measure the electron drift mobility in the c' direction of single-crystal naphtalene from 54 to 324 K. Below 100 K the mobility rises exponentially with decreasing temperature, an effect which we attribute to the onset of band-type motion limited by optical-phonon scattering. This observation allows the identification of the approximately constant mobility at higher temperatures ($T > 100$ K) with the hopping of localized charge carriers.

In this Letter we report the first extension of drift mobility measurements for crystalline molecular insulators to temperatures below 77 K. Our measurements reveal the important result that for naphthalene the electron drift mobility rises dramatically from its (approximately constant) high-temperature value as T is decreased below 100 K. We interpret this observation as the the long-anticipated[1-3] but previously unobserved transition from hopping to band-type motion. This observation of a transition from a roughly constant hopping mobility to one which increases with decreasing temperature is a direct confirmation of the existence at low temperatures of semiconductor (i.e., band) -like mobilities in molecular solids, an effect essential to earlier interpretations of cyclotron resonance[4] in anthracene and the dc conductivities[5,6] of quasi one-dimensional salts based on TCNQ (tetracyanoquinodimethane).

The mobilities for electrons in the c' direction of naphthalene from 54 to 324 K are shown in Figs. 1 and 2. Three regions can be distinguished. From 150 to 324 K the mobility is essentially independent of temperature, similar to the behavior of the electrons in the c' direction of anthracene.[7,8] Writing the temperature dependence as T^n, we find $n = 0.1 \pm 0.1$. Below 150 K the mobility initially decreases by about 10% as shown in

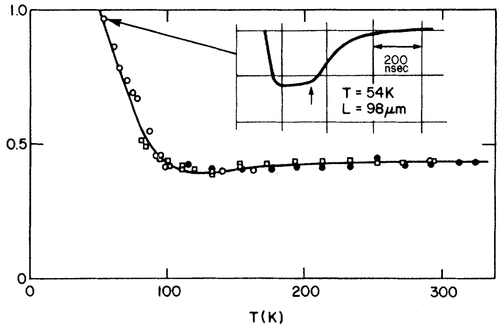

FIG. 1. The mobility, as measured by transient photoconductivity techniques, of electrons in the c' direction of naphtalene from 54 to 324 K. At low temperatures the mobility is exponentially increasing with temperature (see Fig. 2). The different symbols represent measurement of different samples (which have been normalized to 0.44 cm^2/V$\cdot$sec at room temperature). A Janis 8DT He Dewar was used to make measurements below 140 K and a Stratham SD14 was used to make measurements above 77 K (both having control to ± 0.1 K). A "current" mode pulse at 54 K with the transit time marked by an arrow is shown in the inset. The smooth curves drawn through the data (in Figs. 1 and 2) indicate the features of the data which were reproducible among all our samples.