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Electron Tunneling into Intermediate-Valence Materials

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Electron tunneling spectra of TmSe, SmS, SmB₆, and CePd₃ have been measured with the GaAs Schottky-barrier probe tunneling method. Antiferromagnetic TmSe shows an energy gap 2Δ (full width at half maximum) = 1.2 meV, *in situ* pressure-transformed metallic SmS exhibits a gap of 1.7 meV, and SmB₆ shows a gap of 2.7 meV, which is independent of magnetic field. For CePd₃ an inelastic excitation is found near ± 14 meV, which is absent in YPd₃.

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The interaction of localized $4f$ states with conduction-band states at the Fermi level E_F in intermediate-valence (IV) materials raises fundamental questions concerning the nature of the low-temperature coherent ground state and its low-energy excited states. A central issue in recent research concerns the possibility of an insulating singlet ground state.¹ Although electron tunneling spectroscopy appears to be extremely well suited for probing the low-energy excitations in the immediate vicinity of E_F , measurements have only been performed on SmB₆.²

We report on electron tunneling investigations of IV materials using the GaAs Schottky-barrier probe tunneling method.³ We have found well-defined energy-gap structures in the tunneling spectra of antiferromagnetic TmSe, of SmB₆, and of *in situ* pressure-transformed metallic SmS. While the gap of SmB₆ is insensitive to magnetic fields, it disappears in TmSe for field-induced ferromagnetic spin alignment. No such pronounced gaplike structure has been found in CePd₃, which exhibits an inelastic excitation near ± 14 meV.

In certain IV materials, such as SmB₆, SmS, or TmSe, the low-temperature resistivity increase, partly affected by sample purity and stoichiometry, has been subject to various conjectures in terms of gaps due to hybridization or antiferromagnetism, impurity or Kondo scattering, Anderson localization, or Wigner lattice formation.^{1,4,5} Deviations at the lowest temperatures from an activated resistivity behavior have been attributed to extrinsic effects,⁶⁻⁸ partly in view of theoretical predictions⁹ of gaps in the low-energy excitation spectrum of IV states us-

ing, e.g., the Anderson lattice model.^{1,10,11} On the other hand, the above materials can be contrasted with the majority of IV materials which show a decrease of the resistivity at low temperatures, like for instance the intermetallic CePd₃.¹²

We have applied the GaAs probe tunneling method,³ which overcomes inherent difficulties in fabricating oxide barrier tunnel junctions. We have measured the differential resistance $R' = dV/dI$ versus the applied bias voltage V up to ± 100 meV at temperatures between $1.5 < T < 4.2$ K and in magnetic fields up to 20 kOe. Reproducible, symmetric tunneling spectra were obtained only after carefully removing surface contaminants by an *in situ* (within liquid helium) sputter cleaning method.³ The preparation of single crystals of SmS, YSe, and TmSe,¹³ and of SmB₆ (Ref. 14) has been described elsewhere. The annealed polycrystalline CePd₃ ($\rho/\rho_0 = 5$) and YPd₃ samples have been prepared by E. Cattaneo, Universität Köln.

The proper handling of the tunneling and sputtering techniques has been tested with appropriate reference materials. The inset of Fig. 1 shows R' versus V of a cleaved (100) face of superconducting YSe ($T_c = 4.0$ K¹⁵). The tunneling spectrum at 1.55 K shows a BCS-defined gap at $R' = R'_{\max}(V=0) - 0.9 [R'_{\max}(V=0) - R'_{\min}(V \neq 0)]$ of $2\Delta = 1.34$ meV, with $2\Delta/kT_c = 3.9$ exceeding the BCS weak-coupling limit 3.52.

A cleaved (100) face of nominally stoichiometric TmSe ($a_0 = 5.705$ Å) shows at 4.2 K a structureless tunneling resistance ($R' \approx 900 \Omega$) as shown in Fig. 1. Just below the Néel temperature $T_N = 3.5$ K (Ref. 13) we observe a tunneling spectrum similar to that of YSe but with $R'(V$

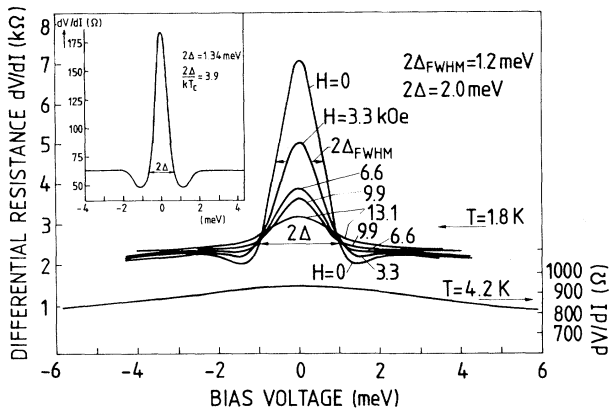


FIG. 1. Tunneling spectrum of a cleaved (100) face of TmSe at 4.2 and 1.8 K, the latter as a function of magnetic field H . Inset: Tunneling spectrum of superconducting YSe ($T_c=4.0$ K) at 1.55 K, with a BCS-defined gap 2Δ .

$= 0$, $H = 0$) = 7 k Ω . We deduce an energy gap $2\Delta = 1.2$ meV at full width at half maximum (FWHM), i.e., replacing 0.9 in the above definition by 0.5. To stress the quantitative difference between TmSe and superconducting YSe we quote also a BCS-defined gap for TmSe $2\Delta = 2.0$ meV. The resistance minimum of TmSe near ± 1.4 meV has disappeared for $H_{\perp} = 6.6$ kOe. The tunneling spectrum becomes field independent above $H_{\perp} = 13.1$ kOe in the same way as the dc resistivity.¹⁶ We conclude that in the ferromagnetic phase of TmSe ($H_{\perp} \geq 13$ kOe¹⁶) the energy gap has disappeared since our gap definition breaks down because of the monotonically decreasing R' with increasing $|V|$. The shape of the spectrum in Fig. 1 for $H_{\perp} \geq 13$ kOe is attributed to a zero-bias anomaly of ferromagnetic TmSe due to electron-magnon interaction.¹⁷

Because of the 1.2 meV gap of TmSe for $T < T_N = 3.5$ K and $H = 0$ we disagree with the interpretation^{18,19} that the 10 meV excitation^{19,20} found in neutron scattering below 50 K results from excitations across the hybridization gap.

Figure 2 shows the tunneling spectrum of a SmB₆ single crystal at 2.0 K. At $H = 0$ we deduce an energy gap 2Δ (FWHM) = 2.7 meV, which is within ± 0.3 meV practically independent of magnetic field up to 15.3 kOe. Note that this gap is still defined for $H \neq 0$ since $R'_{\min}(V \neq 0)$ is constant up to ± 60 meV. ($2\Delta = 4.9$ meV at $H = 0$ is quoted for comparison.) Changes in $R'(V = 0)$ with magnetic field, however, cannot be accounted for by the rather small negative magnetore-

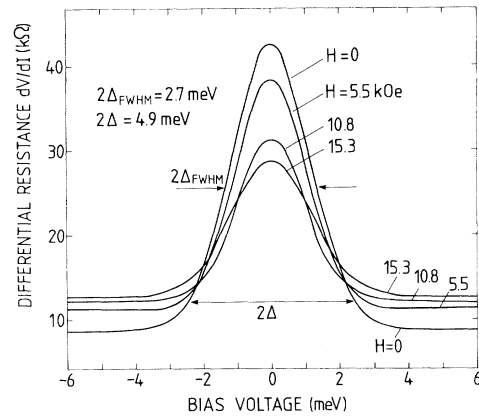


FIG. 2. Tunneling spectrum of a single crystal of SmB₆ at 2.0 K as a function of magnetic field H_{\perp} .

sistance.²¹ We find that $R'(V = 0)$ is strongly reduced by excessively pressurizing the GaAs-SmB₆ contact.

For SmB₆ a Wigner-crystal localized state with a large gap of about 160 K (14 meV) has been invoked,²² which, however, is not supported by our tunneling results.

The effective pressure in a GaAs-probe point-tunneling experiment can actually reach the yield pressure of the sample surface.³ This unique opportunity has been exploited for tunneling into the pressure-transformed metallic IV-phase of SmS. Figure 3(a) shows the tunneling spectrum of a cleaved (100) face of SmS at 4.2 K in its semiconducting ("black") phase showing a structureless

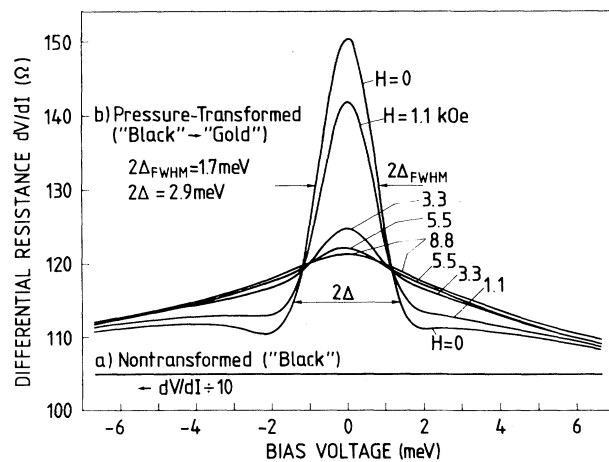


FIG. 3. Tunneling spectrum of a cleaved (100) face of SmS at 4.2 K: (a) semiconducting ("black") phase, (b) *in situ* pressure-transformed metallic ("gold") IV phase as a function of magnetic field H_{\perp} .

$R'(V) \approx 1 \text{ k}\Omega$. Gradually pressurizing the SmS surface by the GaAs tip exhibits abruptly a tunneling spectrum with a well pronounced gap $2\Delta(\text{FWHM}) = 1.7 \text{ meV}$ as shown in Fig. 3(b), with $R'(V=0, H=0) = 150 \Omega$. The size of this gap remains unchanged upon further pressurizing SmS, with a change in R' up to only 5%. The magnetic field dependence of the tunneling spectrum saturates beyond a field of 8.8 kOe, for which the gap can no more be defined (see above). A very similar tunneling spectrum is obtained for mechanically polished ("gold") SmS [$2\Delta(\text{FWHM}) = 2.1 \text{ meV}$] showing the same magnetic field dependence. The unexpected⁸ magnetic field dependence of the gap of metallic SmS may be due to magnetoresistance effects in the remaining non-transformed divalent SmS²³ outside of the point-contact region.

Asymmetric tunneling spectra have been obtained with SmB₆-oxide-Pb junctions.² A rough estimate of $2\Delta(\text{FWHM}) \approx 10 \text{ meV}$ (based on our definition) is four times larger than our value. In our experiments when making contact to the SmB₆ surface without sputter cleaning we observe very similar spectra. The asymmetry in our case is attributed to leakage resistance, which is tunneling assisted by intermediate states due to surface contamination. It is possible that the oxide barrier of the SmB₆-oxide-Pb junctions² may not have been continuous throughout the junction.

The tunneling spectrum of CePd₃ at 4.2 K in Fig. 4 exhibits an inelastic excitation near $\Delta' = \pm 14 \text{ meV}$ which is independent of magnetic fields up to 15 kOe and is absent in YPd₃. This excitation can be correlated with a resonant scattering process of conduction electrons at empty $4f^1$ states 14 meV above E_F as identified in an analysis of far infrared data,²⁴ including those of Pinkerton.²⁵ Interestingly enough, we also observe the 14-meV excitation in asymmetric $R'(V)$ characteristics of Ga-CePd₃ (metal-metal) point con-

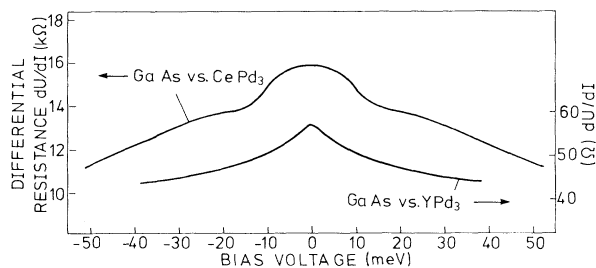


FIG. 4. Tunneling spectrum of polycrystalline CePd₃ and YPd₃ at 4.2 K.

tacts, which can also be formed *in situ* by our method. This excitation is found for only one polarity of V for electrons injected into CePd₃.

The characteristic features of our tunneling spectra seem to correlate qualitatively with the low-temperature resistivity behavior. The gap of TmSe appears to be primarily spin-superstructure induced. The tunneling spectrum of CePd₃ may qualitatively be considered as a broadened version of the pronounced spectra of SmB₆ and SmS. Our results raise fundamental questions about the nature of the gaps in IV materials and about what is observed by electron tunneling. Since the electronic density of states of IV materials is believed to be asymmetric around E_F , as for instance inferred from asymmetries in metal-metal point contact spectra,²⁶ it is surprising that we observe symmetric tunneling spectra in all materials. Instead of involving the one-electron density-of-states picture we propose a description of our spectra in terms of a more adequate particle representation. We consider Δ' and Δ [corresponding more closely to Δ' than $2\Delta(\text{FWHM})/2$] as the quasiparticle excitation energies of bound electron-hole pairs, with $2\Delta'$ or 2Δ the electron-hole binding energy. For these electron-hole pairs a symmetric tunneling characteristic is obtained by either condensing ($e^- + 4f^{n-1} \rightarrow 4f^n$) or breaking ($4f^n \rightarrow 4f^{n-1} + e^-$) pairs, in analogy to the Cooper-pair tunneling mechanism in superconductors. $1/2\Delta'$ or $1/2\Delta$ is assumed to be a measure of the electron-hole lifetime τ_{eh} , which on the other hand is determined by the charge relaxation rate $\tau_{eh} \sim 1/\Gamma_c$. Indeed, the roughly five times larger $2\Delta'$ of CePd₃ compared to 2Δ of IV SmS or SmB₆ is consistent with the approximately five times larger Γ_c of CePd₃ in comparison to IV SmS or SmB₆.²⁷ Consequently the "broadened" tunneling spectrum of CePd₃ compared to the pronounced one of SmB₆ or SmS is ascribed to the shorter τ_{eh} in CePd₃.

In the case of SmB₆ our interpretation is supported by recent far-infrared transmission measurements of a gap of similar magnitude.²⁸

In metal-metal point-contact spectroscopy between Mo and SmB₆ (or TmSe) the resistance peak at zero voltage has been interpreted by analogy to tunneling experiments of SmB₆ (Ref. 2) as signature of a narrow gap.²⁹

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