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Intermediate Valence Compounds

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Intermediate valence, or homogeneous mixed valence, occurs in certain rare-earth compounds such as CePd₃, SmS, EuPd₂Si₂, TmSe, and YbAl₂ where the rare-earth valence is intermediate between two integral values, i.e., fractional. There are three key characteristics of these solids: the crystal

density is unusually sensitive to changes in temperature and/or pressure; the low-temperature susceptibility is finite; and the coefficient of the linear term in the low-temperature specific heat is enhanced (the heavy-fermion compounds are a related class of materials).

Rare-earth elements have an electronic configuration consisting of a filled xenon core, 2–4 bonding (valence) electrons in 5*d* and 6*s* states, and 0–14 4*f* electrons. The configuration can be expressed as (5*d*6*s*)^z4*f*ⁿ, where *z* is the valence and *n* the 4*f* count. In the solid state the bonding electrons form energy bands. The 4*f* orbital has a small radius and does not contribute directly to the bonding. In ordinary rare-earth compounds the 4*f* behaves as a localized orbital, with a well-defined magnetic moment. Ordinarily the energy separation $E = E_n - E_{n-1}$ between configurations (5*d*6*s*)^z4*f*ⁿ and (5*d*6*s*)^{z+1}4*f*ⁿ⁻¹ is large (5–10 eV); for compounds of the elements Ce, Sm, Eu, Tm, and Yb the separation can be much smaller (0–2 eV). Under these circumstances an interaction which hybridizes the two configurations via a process where the conduction electrons hop on and off the rare-earth sites can cause them to fluctuate between the 4*f*ⁿ and 4*f*ⁿ⁻¹ configurations. This leads to a quantum-mechanical ground state which contains an admixture of both configurations. The strength of this mixing interaction is given by $\Gamma = V^2 N(E_n)$, where *V* is the matrix element of the interaction and *N*(*E*_{*n*}) is the number of conduction electron states per unit energy interval. The degree of admixture depends on the ratio *E*/Γ; when this is small, both states contribute equally and the valence is nonintegral (near *z* + ½). In these compounds the valence has the same fractional value at each rare-earth site. This is referred to as homogeneous mixed valence to distinguish it from inhomogeneous mixed valence where the rare-earth element has different values of integral valence at different lattice sites. This latter case occurs in compounds such as Sm₂S₄ and Fe₃O₄.

The radius of the 4*f* ion in the 4*f*ⁿ state is larger than that of the 4*f*ⁿ⁻¹ state. The lattice constant of a given compound will thus be larger for the 4*f*ⁿ case than for the 4*f*ⁿ⁻¹ case. At ambient pressure, SmS contains divalent Sm; but at elevated pressure, SmS converts to an intermediate valence phase. The lattice constant is intermediate between that expected for divalent and trivalent SmS (Fig. 1). A lattice constant deviation is a signature of mixed valence. The fractional valence can be estimated by assuming the lattice constant varies linearly with valence.

This ability of the 4*f* ion to change size lies behind the above-mentioned extreme sensitivity of the crystal density (or lattice constant) of many mixed valence compounds to changes in temperature and pressure. In two cases (SmS and elemental Ce metal) this leads to an unusual kind of phase transition, namely, an *isomorphic* transition where at the transition pressure the lattice constant undergoes a large (5%) discontinuous decrease without any change in the crystal symmetry; further at a critical temperature and pressure the compressibility and thermal expansion coefficients diverge. These are valence transitions where the 4*f* count decreases causing the ions to shrink. In other materials no such phase transition is observed, but the thermal expansion is large and highly temperature dependent.

The isomer shift measured in a Mössbauer experiment

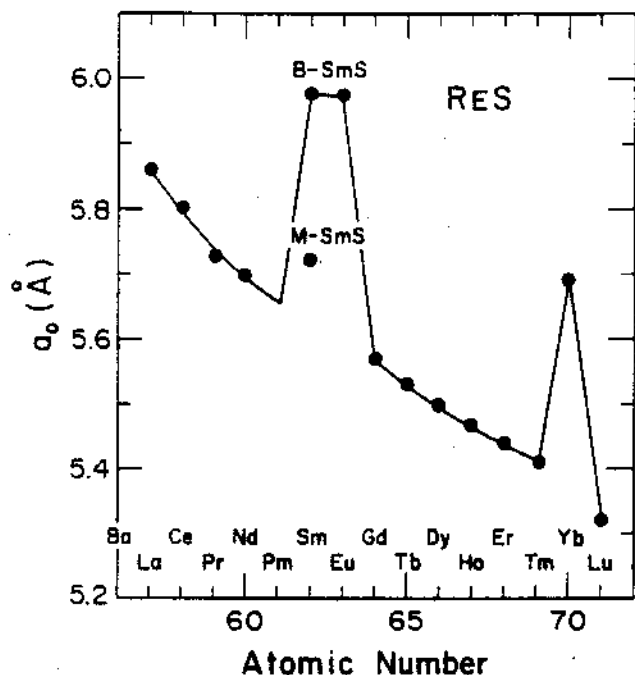


FIG. 1. The lattice constants versus atomic number for the rare-earth sulfides. In B-SmS, EuS, and YbS the rare earth is divalent; in M-SmS the Sm is in an intermediate valence state; for all other cases the rare earth is trivalent.

measures the electron density at the nucleus. This differs for the two configurations $4f^n$ and $4f^{n-1}$ because the extra $4f$ electron increases the screening of the nucleus seen by the outer valence electrons and hence decreases the probability for finding them at the nucleus. For homogeneous mixed valence Sm and Eu compounds, a single isomer shift is observed intermediate between that observed for divalent and trivalent compounds. For inhomogeneous mixed valence compounds two isomer shifts are observed, at the values expected for the integral valence states.

The lattice constant and isomer shift measure properties of the ground state and therefore yield one (intermediate) value for homogeneous mixed valence compounds. Other experiments measure properties of highly excited states, and the signatures of both integral valence states are observed. An important example is x-ray absorption. The L_{III} absorption edge occurs when the photon energy equals the value necessary to excite a $2p$ deep core electron to the valence band. For a rare-earth ion in the $4f^{n-1}$ configuration about 8–10 eV more energy is required to unbind the $2p$ electron than for the $4f^n$ case. Again, this is due to screening effects by the extra $4f$ electron. In mixed valence compounds two absorption edges are observed, at the values expected for the two integral valence cases. This is because each component of the hybridized wave function couples to a different integral-valent excited state. The intensity of the two absorption peaks can be used to estimate the valence; indeed, this is presently considered to be the best way to determine valence.

A very important property of these compounds is that the thermodynamic behavior is a universal function of a scaled

temperature. For several compounds the magnetic susceptibility $\chi(T)$ (Fig. 2) has the same shape: a maximum at a temperature T_* ; a low-temperature value proportional to C/T_* , where C is the Curie constant (the upturn at low temperature is not an intrinsic property but is an impurity effect); and a high temperature law $C/(T + 2T_*)$. For all cases the product $T\chi(T)/C$ has exactly the same dependence on T/T_* ; this property is called *scaling*. Simultaneously the specific heat at low temperatures has a linear temperature dependence with coefficient γ proportional to $1/T_*$. The thermal expansion coefficient typically shows a maximum near the characteristic temperature. The inelastic neutron-scattering spectrum (which measures the energy required to flip a $4f$ spin) has a maximum at an energy $k_B T_*$. The characteristic temperature T_* has values between 10 and 2000 K for different compounds and can be varied in a given compound by pressure or alloying. There is a correlation between T_* and valence; e.g., in cerium compounds, large T_* corresponds to smaller f count.

For a conventional rare earth with a well-defined local moment the susceptibility should diverge as $T \rightarrow 0$. For intermediate valence materials the susceptibility is finite as $T \rightarrow 0$; for Ce, Sm, and Yb, $\chi(T)$ is intermediate between the values expected for the integral valence cases (Fig. 2b). The local moment is *quenched*; finite susceptibility (Pauli paramagnetism) is characteristic of nonmagnetic metals. This and the fact that the low-temperature specific heat has a linear temperature dependence implies that the low-temperature behavior is that of a *Fermi liquid*. That is, despite the extremely complicated interactions between the conduction electrons and the $4f$ ions, in the ground state the conduction electrons behave as though they are noninteracting.

The theory which describes mixed valence compounds is based on the Anderson model. This describes a single $4f$ impurity embedded in a nonmagnetic host. The energy separation $E = E_n - E_{n-1}$, the hybridization V , and the density

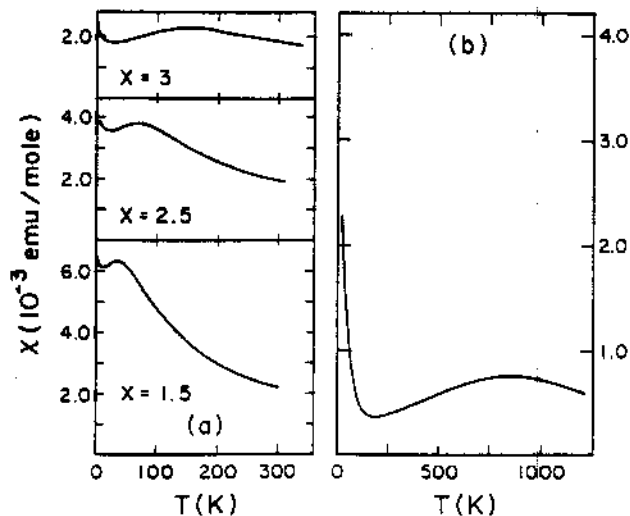


FIG. 2. (a) Susceptibility for three concentrations x of $CeN_{1-x}Sn_x$. (b) Susceptibility of CeN . The line indicates the susceptibility for a trivalent Ce ion; the susceptibility of a tetravalent cerium ion is essentially zero.

of states $N(E_n)$, as well as the energy separation $U = E_{n+1} - E_n$, are taken as model parameters. For the rare earths U is typically 6 eV; V is of order 0.1 eV and E varies from close to zero for Sm, Eu, Tm, and Yb mixed valence compounds to 2 eV for cerium. The model predicts the above-mentioned universality: the characteristic temperature T_* is proportional to the so-called Kondo temperature T_K which is computed in the model. This is the energy scale for fluctuations of the $4f$ spin. The local moment is quenched by these spin fluctuations whose ultimate origin lies in the fluctuations between the two integral-valent configurations. The ground state is thus a singlet and the enhanced specific heat coefficient arises from thermal excitation of spin fluctuations. The predictions of the model depend on the orbital degeneracy of the rare-earth integral valence states (e.g., 6 for the Ce $J = 5/2$ state and 8 for the Yb $J = 7/2$ state). The susceptibilities shown in Fig. 2 are computed precisely in the model, as are the inelastic neutron-scattering spectra, the linear coefficients of specific heat, and the dependence of the valence (and hence lattice constant, or thermal expansion) on temperature. Confidence in the application of the Anderson model to these materials has been significantly increased by recent photoemission and inverse photoemission experiments. These essentially measure the model parameters E , U , and V , eliminating unknown parameters and allowing direct calculation of the thermodynamic quantities.

The Anderson model describes an impurity, whereas mixed valence compounds consist of a periodic lattice of $4f$ sites. For temperatures of order T_K or larger the model adequately describes the data, implying that the $4f$ ions behave as a set of noninteracting impurities. At lower temperatures this is not the case, and interactions among the $4f$ ions affect the behavior. Properties such as susceptibility, specific heat, and neutron spectra show deviations from the single-impurity predictions at low temperatures. For Ce, Yb, and Eu compounds the resistivity (which is large and finite for an Anderson impurity) vanishes as $T \rightarrow 0$. This buildup of interactions, the vanishing of the resistivity, and the onset of Fermi liquid behavior is referred to as *coherence*. Such coherence is observed most convincingly in de Haas-van Alphen experiments, which show that the wave functions in the ground state are not random (as they would be for impurity scattering) but fully periodic. The description of coherence on the theoretical level requires an Anderson lattice model. This is an extremely difficult problem at the present time. Future work on the mixed valence problem will stress the development of coherence, which is as yet poorly understood.

The ground states of Sm and Tm compounds are not always metallic. In the intermediate valence state, SmB_6 appears to be an insulator with an extremely small energy gap, of order 0.01 eV as compared to 1–10 eV in ordinary semiconductors. One expectation is that the Anderson lattice model can lead to the development of a hybridization-induced energy gap at low temperatures; hence the model should prove capable of describing these unusual semiconductors as well as the Fermi liquid compounds.

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