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X-Ray Absorption Study of Mixed-Valence TmSe

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The L_{III} x-ray absorption edge of Tm in TmSe yields a temperature-independent valence of 2.58 ± 0.07. The thermal damping of the extended x-ray absorption fine structure of TmSe is nearly identical to that of ErSe. This indicates very weak coupling of breathing shell charge fluctuations of the Tm ions to the phonons and very little static disorder of the lattice.

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In this Letter we wish to report on L_{III} x-ray absorption spectra of mixed-valence TmSe and several integral-valence reference compounds. The study was undertaken to test the potential of x-ray synchroton radiation for mixed-valence research in general and to address two controversial aspects of the physics of TmSe in particular. X-ray absorption should be a powerful tool in mixed-valence research for two reasons: First, one can measure the ratio of both configurations (the valence) through the structure of the spectrum within a few electronvolts around the absorption edge.[1] Second, one can obtain the instantaneous distribution of radial distances to the neighbors of the unstable $4f$ ions, averaged over the sample, from an analysis of the extended x-ray absorption fine structure (EXAFS). This distribution gives, e.g., information about microscopic dynamic disorder of the lattice due to coupling of valence fluctuations to phonons. Both measurements can be done over a wide range of temperatures, pressures, and concentrations.

Although TmSe is probably the most extensively studied mixed-valence compound,[2] there is still controversy over the fractional valence, and, more importantly, it is uncertain whether the ground-state configurational mixture is dynamic or static. In well-characterized stoichiometric samples the valence is near 2.75, if deduced from the lattice constant at room temperature,[2] or near 2.55, when deduced from the Curie constant or from the magnetic neutron cross section above 70 K.[3] The dynamic nature of the low-temperature mixture is inferred from circumstantial evidence[2] but cannot be verified directly by Mössbauer isomer shift, which is very small for Tm and overshadowed by large hyperfine splittings.

The magnetic fluctuations, while being fast and temperature independent above 70 K, slow down linearly with decreasing temperature below 70 K and eventually are slow enough to admit magnetic order below 3 K,[4] which is in the range of magnetic ordering temperatures for normal, stable-valence Tm compounds (e.g., TmS). The low-temperature resistivity of stochiometric samples points to an insulating ground state.[5] Thus, while there is circumstantial evidence to the contrary,[2] there are also strong arguments for a static valence mixture in TmSe at $T \to 0$ K.

The uncertainties about the ground state of TmSe illustrate the need for experimental evidence of configurational motion of mixed-valence materials which goes beyond the magnetic fluctuations, namely, to charge fluctuations. The most prominent charge fluctuation associated with configurational motion is the radial breathing motion of the outer (5*d*6*s*) valence electrons which is driven by fluctuations of the effective nuclear charge of the unstable rare-earth (RE) ion when the 4*f* occupation number fluctuates by 1. Its effect on the nearest-neighbor positions could be as large as the change of the RE ionic radius in static integral-valence compounds ($\Delta r = 0.16$ Å between Tm^{2+} and Tm^{3+}). Recent measurements have detected large phonon anomalies due to such breathing shell motion in $Sm_{1-x}Y_xS$.[6,7] The time scale τ_c of the charge fluctuations is expected to be of the order of that of the magnetic fluctuations τ_m, or longer. Therefore, in TmSe, where $\tau_m \sim 10^{-13}$ sec abive 70 K (Ref. 3), τ_c is slow enough to allow strong coupling of the breathing shell charge fluctuations to the phonons. Such coupling will of course also depend on lattice symmetry and on the valence. Judged from the behavior of the magnetic fluctuations, the charge fluctuations should be incoherent (uncorrelated between ions in space and time) at least above 70 K. They should therefore cause local dynamic disorder of the nearest-neighbor positions, which should have a strong damping effect on the EXAFS, in addition to the normal damping due to zero-point motion and finite-temperature incoherent phononic motion. In a more coherent charge fluctuation of this type, one may expect beats of the EXAFS due to the enhanced statistical weight of two nearest-neighbor shells with slightly different radii. Such an effect is also expected in static mixtures with certain specific configurational ratios.

The French synchrotron facility Laboratoire pour L'Utilisation du Rayonnement Electromagnêtique at Orsay provided the x-ray beam, emitted by 1.72-GeV electrons in the ring D.C.I. An energy resolution of 2–3 eV was achieved with a (220) silicon monochromator. Intensities were measured before and after the sample through conventional ionization chambers. The samples were powdered and held on Scotch tape. Several sample thicknesses were studied in order to check on the influence of beam harmonics, which turned out to be negligible. The lattice parameters of the samples are 5.711 ± 0.003 Å for TmSe, 6.335 ± 0.005 Å for TmTe, and 6.031 ± 0.005 Å for ErSe.

Figure 1 shows the structure of the Tm L_{III} absorption edges in TmS, TmSe, and TmTe. The difference between the absorption curve before the edge and the mean absorption averaged over the EXAFS oscillations after the edge is normalized to 1. The L_{III} edge of Tm^{3+} in TmS presents a strong peak, which is a few electronvolts wide. Such a peak also appears at the L_{III} edge of Er^{3+} in ErSe and there is little difference in the two shapes. The peak is in fact a general feature of L_{III} edges for all RE atoms in 2^+ and 3^+ valence states, and is largely due to transitions into empty 5*d* states. The valence of Tm at atmospheric pressure is 2^+ in TmTe, when the sample is

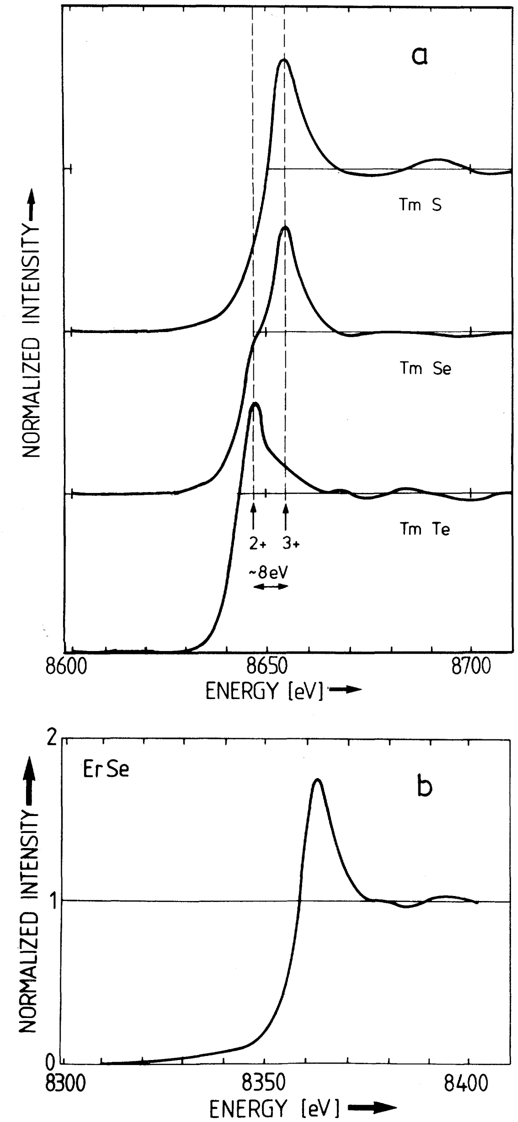

FIG. 1. L_{III} absorption edge for Tm in TmS (valence $v \simeq 3$), TmSe ($v \simeq 2.58 \pm 0.07$), and TmTe ($v \simeq 2$) at 300 K. Note shift of edge by 8 eV between $v = 2$ and $v = 3$. The shape of the edge of TmSe does not depend on temperature between 300 and 10 K.

stoichiometric which is a difficult condition to achieve. The L_{III} edge of our best sample, shown in Fig. 1, has nearly the same shape as that of Tm in TmS, but is shifted by nearly 7 eV towards lower energy. A similar shift is observed between Sm^{2+} and Sm^{3+} (Ref. 1) and between Yb^{2+} and Yb^{3+} (Ref. 8). This shift occurs because the energy of the transfer of an electron from the $2p$ shell inside the $4f$ shell to the $5d$ shell outside depends on the intervening $4f$ charge. The shape of the Tm edge in TmTe differs slightly from that in TmS; there is a small bump at the energy of the peak for Tm^{3+}, which changes from sample to sample and is apparently due to a small, residual fraction of Tm^{3+}, which depends on sample quality. The L_{III} edge of Tm in TmSe in Fig. 1 shows a peak at the Tm^{3+} energy and a shoulder near the energy of the peak of Tm^{2+}. Analysis of this spectrum by fractional superposition of either the spectra (shifted with respect to each other by 8 eV) yields a TmSe a Tm^{2+} concentration of (42 mainly due to the stoichiometry problem of the TmTe. Even so, our measurement is in clear disagreement with the valence deduced from the lattice constant but agrees quite well with magnetically determined values. We have studied the TmSe spectrum as a function of temperature and find that *between 300 and 10 K the valence remains constant within 1%*.

Figure 2 presents the EXAFS above the L_{III} edges of Tm and Er in TmSe at 300 and 20 K. The spectra are quite similar at the same temperature and clear damping is observed at 300 K in both compounds.

The physical information obtainable from the EXAFS has been discussed in many papers.[9] Fourier filtering was used to isolate the contribution from the nearest-neighbor (nn) shell. The argument of this nn oscillation yields the *mean* Tm-Se *distance*, if the phase shifts in the absorbing atom and in the nearest neighbors are known. These phase shifts have been shown to be insensitive to the outer valence electrons[10] and are therefore transferable between compounds without regard to valence (note that they do not provide any information about the valence charge distribution itself). With use of the EXAFS of the ErSe reference compound to obtain the phase shift from the known lattice constant, the TmSe EXAFS yields the correct Tm-Se distance within the usual 0.01-Å accuracy of EXAFS. This indicates that our data are not affected by spurious effects of disorder.[11]

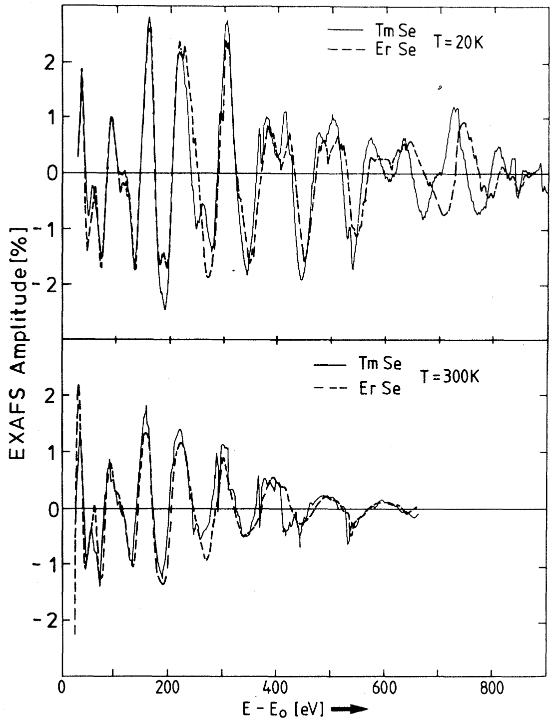

FIG. 2. EXAFS of Tm in TmSe and Er in ErSe above the L_{III} edge at 20 and 300 K. The amplitude is expressed in percentage of the intensity step of the absorption edge. Note the similarity of the spectra of the IV compound with its reference compound—in particular, the nearly identical thermal damping.

Information about the distribution of the nearest neighbors around the mean distance is obtained by analysis of the energy or k dependence of the nn oscillation (k is the wave vector of the emitted electron, defined by $E \equiv \hbar^2k^2/2m$, with $E=0$ at the edge). The envelope of the Fourier-filtered nn contributions to the EXAFS are nearly the same for ErSe and TmSe, at both temperatures (see Fig. 2). At 20 K there are some deviations from sample to sample (e.g., a shallow dip near $k \simeq 8$–10 Å^{-1}), but these deviations never exceed 20%. If there were two nn Tm-Se distances in a sample differing by Δr, and if they occurred with relative ratio R, the Fourier-filtered contribution of the nn shell would be multiplied by $[1+R^2+2R\cos(2k\Delta r)]^{1/2}$.[12] This factor causes beats with a first minimum near $k \simeq 10$ Å^{-1} (for $\Delta r \simeq 0.16$ Å), which lies in the middle of our range of k's. We can put an upper limit of $R < 5\%$ to our best spectra and find $R \simeq 25\%$ in our worst case. It follows that the Tm nn-shell radial distribution function in TmSe peaks around a single value just as that of Er in ErSe, or that *the Tm atoms all have statistically equivalent environments*. This conclusion holds within the above scatter of the data between samples. At the same temperature the Fourier-filtered nn EXAFS contributions are in fact nearly identical over the entire range of accessible k's for ErSe and TmSe. There is no additional damping of the EXAFS of TmSe. This means that *there is no special positional disorder in TmSe relative to ErSe, static or dynamic.* If we assume the harmonic approximation, the damping results in a factor $\exp(-2\sigma^2k^2)$ multiplying the EXAFS. If we plot the logarithm of the ratio of the envelopes at 300 and at 20 K against k^2, we obtain a linear relationship from which we extract $2\sigma^2(300\text{ K}) - 2\sigma^2(20\text{ K}) = (0.008 \pm 0.0004)$ Å^2, for both ErSe and TmSe. The agreement for our one pair of samples is so perfect that we suspect it to be somewhat fortuitous, in view of the above-mentioned deviations of the spectra from sample to sample. The thermal mean square excursion of the TmSe distance is then at least 0.09 Å at 300 K, somewhat smaller than the difference of ionic radii of Tm^{2+} and Tm^{3+}. If an incoherent breathing motion of the $5d6s$ shell of the Tm ions caused a corresponding random radial displacement of the atoms of the nn shells, this motion would have been detected easily by damping of the EXAFS, especially at 20 K, where the damping in TmSe would then have been three times stronger than in ErSe at 300 K.

Quite obviously there are no significant differences in the EXAFS of the mixed-valence compound TmSe and the integral-valence reference compound ErSe. In particular, TmSe does not seem to decompose into a static mixture of Tm^{2+} and Tm^{3+} with different radii at low temperatures and on the other hand no coupling of the breathing shell charge fluctuation to phonons is noticeable by EXAFS as it was noticeable by neutrons in $\text{Sm}_{1-x}\text{Y}_x\text{S}$.[6] It is worth noting that with a ratio of $\text{Tm}^{2+}/\text{Tm}^{3+} \simeq 1$, as obtained from the structure of the edge, it is impossible to construct any instantaneous distribution with two Tm neighbor shells of different radii in the NaCl structure. Thus with this value of the valence, symmetry excludes a static mixture with different nn shell radii and coupling of the phonons to a coherent breathing charge density wave. Presumably, it also strongly reduces coupling to random breathing motion at high temperatures. It should also be noted that since $\tau_c > \tau_m$, we must have $\tau_c > 2.5 \times 10^{-12}$ sec at 20 K if one regards the width of the quasielastic line of the magnetic fluctuation spectrum as representative of τ_c^{-1}, or $\tau_c > 4 \times 10^{-13}$ sec if one includes the inelastic part of that spectrum; in both cases $\tau_c > \tau_{\text{phon}}$. Thus, in spite of being energetically allowed, drastic phonon anomalies due to valence fluctuations are not the rule in mixed-valence compounds. The anomalies found in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ seem to be due to critical charge fluctuations tied to the phase boundary in the temperature-driven valence transition.[6,7]

The question of the ground state of the TmSe remains open. The nature of a possible static mixture, if any, was narrowed down to an arrangement in which the Tm^{2+} and Tm^{3+} $5d6s$ shells and the Se valence electrons distort coherently such that the NaCl structure is preserved, with positional nn fluctuations much smaller than the maximum possible value expected on the basis of the naive picture of two kinds of hard-sphere ions with radii differing by 0.16 Å. A careful study of stoichiometry effects would be needed to detect such a coherent static mixture or an analogous dynamic mixture by EXAFS. Obviously, experiments with different local symmetry, especially in dilute alloys, will be very instructive.

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Extended X-Ray-Absorption Fine-Structure Studies of Electron-Lattice Correlations in Mixed-Valence $Sm_{0.75}Y_{0.25}S$

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X-ray absorption spectrum of the Sm L_{III} edge has been measured in mixed-valence $Sm_{0.75}Y_{0.25}S$. From analysis of the edge structure and extended x-ray absorption fine structure, the valence is determined and it is shown that the S neighbors of each Sm atom adopt an average distance rather than a dynamically distorted environment with two distances corresponding to the two valence states. From this it is concluded that the characteristic Sm $4f$-band width is not greatly modified by polaron effects.

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The role of polaron effects[1,2] in homogeneously mixed-valence rare-earth materials[3] has been a subject of speculation due to an almost complete lack of direct experimental information. The possibility of such dynamical electron-lattice correlations in systems like SmS and $Sm_{1-x}Y_xS$ follows from the facts that (1) there is strong f-electron–lattice coupling as exhibited in lattice[3-5] and phonon[6,7] anomalies, and (2) the characteristic energy scale[1-3,5,7,8] Δ, which is the width of the correlated f band[3,5,7,8] or qualitatively the valence fluctuation rate,[3] is in the range $10^{-3} < \Delta < 10^{-1}$ eV, comparable to phonon frequencies ($\hbar\omega \sim 0.03$ eV). We report here x-ray absorption edge and extended x-ray-absorption fine-structure (EXAFS) measurements on mixed-valence $Sm_{0.75}Y_{0.25}S$ which determine directly both the valence and near-neighbor environments of the Sm ions. We find that the lattice around each Sm ion adopts an average position with no pronounced dynamic electron-lattice correlations, and we determine the Sm-S distance which is not simply proportional to the valence. Our results support theoretical treatments of mixed valence as a homogeneous electronic many-body problem[3,7,8] with energies dependent upon average lattice positions but with no qualitatively important dynamic polaron effects.

Coupling of f-electron occupation to changes in the nearest-neighbor distance r is well known in mixed-valence materials[3] and may be described by a Hamiltonian of the form[1-3,7]

$$H = H_{\text{electronic}} + \lambda(a + a^\dagger)f^\dagger f + \hbar\omega(aa^\dagger + a^\dagger a)/2, \qquad (1)$$

where $a^\dagger$ and $f^\dagger$ create phonons and electrons, ω is the phonon energy, and λ is the coupling constant. Assuming the Sm-S distance r varies from 2.98 Å in $Sm^{2+}S$ to ~2.80 Å in $Sm^{3+}S$, Sherrington and von Molnar[1] (SvM) showed that $\lambda = \Delta r(M\hbar\omega/2)^{1/2} \sim 0.06\ \text{eV} \sim 2\hbar\omega$ and that the energy gained from the distortion is $E_\lambda \sim 4\lambda^2/\hbar\omega \sim 0.5$ eV. From polaron theory[9] one finds that $E_\lambda > \Delta$ or

$$4\lambda^2 > (\hbar\omega)\Delta \qquad (2)$$

is the condition for the formation of a strongly coupled polaron system. For such drastic electron-phonon correlations the distribution of nearest-neighbor distances, described by the near-neighbor pair correlation functions $p_2(r)$ and $p_3(r)$ for 2+ and 3+ ions, respectively, would have their peaks separated by $\Delta r = 0.18$ Å. Since the