Table I. van der Waals' and Total Energy Changes: 1 → 2 kcal/mol

R	R′	E_{vdw}	E_{total}
Me	Me	0.07	0.02
Me	*t*-Bu	0.29	0.33
t-Bu	*t*-Bu	0.86	1.07

transformation **1** → **2**. Unfortunately, we are unable to carry out calculations that would model this pathway.

Next, we considered placing methyl groups and *tert*-butyl groups at atoms 1 and 4 or at atoms 1 and 6. If one examines a Dreiding model of the 1,6-di-*tert*-butyl compound, the alkyl groups appear to be much too close together, with the nearest hydrogens being separated by about 1.5 Å. Since the van der Waals' H–H minimum is around 3 Å, this implies large repulsions between the *tert*-butyl groups. This implication is erroneous, however, due to the well-known inaccuracy of Dreiding molecular models. The C–C–C bond angles in COT are 126.1° (experimental[13] and 124.6° (MMP2), while the models show an idealized value of 120°. The difference is quite significant. With the correct bond angle, the *tert*-butyl groups are moved away from one another to the point where there is no repulsion between them but rather attractions between even the nearest hydrogen atoms. The interaction between any pair of atoms is not very large (for two hydrogens at their van der Waals' minumum the interaction energy with the MMP2 force field is −0.06 kcal/mol). Most of the atoms are somewhat further apart than the van der Waals' minimum; thus, most of the interactions are of the order −0.01 kcal/mol per atom pair. But the *tert*-butyl group contains 13 atoms; therefore, for 2 interacting *tert*-butyl groups, there are 169 interactions! Clearly, though the numbers are individually small, their total is significant. In the 1,4-di-*tert*-butyl case, the groups are much farther apart; hence, the total interaction is correspondingly less.

Table I summarizes our calculations for the dimethyl, di-*tert*-butyl, and methyl-*tert*-butyl cases. The van der Waals' attraction is always greater for the 1,6 isomer, and the steric energy correspondingly lower. The trend in van der Waals' attraction energy parallels the total number of interactions between the alkyl groups: 169 for di-*tert*-butyl, 52 for methyl-*tert*-butyl, and 16 for dimethyl. The conclusion is interesting: large groups such as *tert*-butyl, which are quite polarizable, will show large van der Waals' attractions; small groups like methyl, which are not very polarizable, will show extremely small interactions. Of course, the total energy difference between **1** and **2** depends upon other contributions besides the van der Waals' attractions. But these other factors appear to be quite small, and the nonbonded attractions dominate the situation.

Conclusions

Thus, the MMP2 force field clearly indicates **1** to be more stable than **2** in the gas phase. We emphasize that ther are no adjustable parameters in the calculation; this is a necessary result of this force field. The measurements by Streitwieser are in solution, and some change in the equilibrium constant may attend a change to the gas phase. In particular, a difference in molecular volume for the two isomers might alter the experimental value. Since there are no overlapping van der Waals' radii that differ significantly in the two isomers, one might expect this effect to be negligible. Also, the enthalpy difference may be sensitive to differences in the polarizability of the solvent molecules. We believe that experiment and theory are in good agreement. The proposal by Streitwieser that this equilibrium is determined primarily by van der Waals' attraction between the *tert*-butyl groups is borne out by the molecular mechanics calculations.[14]

Acknowledgment. Thanks are due to Professor Streitwieser for informing us of the experimental results prior to publication. Also, discussions of possible modes of solvent effects with Dr. L. L. Shipman have been helpful.

Registry No. **1** (R, R′ = Me), 29554-56-1; **1** (R = Me; R′ = *t*-Bu), 82209-38-9; **1** (R, R′ = *t*-Bu), 76794-05-3.

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[13] Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724.

[14] One of the referees has suggested that the structural parameters for the molecules in this study should be made available. The atomic coordinates for all of these structures are available from the authors upon request.

Electron-Transfer Rates in Mixed-Valence Europium Sulfide by Time Domain Reflectometry

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Abstract: Intervalence electron transfer in a mixed-valence sample of europium sulfide is shown to give rise to dielectric relaxation which can be studied by using the technique of time domain reflectometry (TDR). It is demonstrated that the dielectric relaxation times measured by using these techniques can be directly related to the rates of intervalence electron transfer. Rates obtained via time domain reflectometry are compared with Mössbauer results obtained on the same sample and with other published Mössbauer and conductivity studies. The significance of these results relative to Hush theory is also examined.

Electron-transfer processes are dominant phenomena in a number of important areas in both chemistry and physics such as redox reactions, electrochemistry, and semiconductor science. Understanding the rate at which these processes occur and the energetics which govern both the rate and extent of electron transfer should help scientists to understand and manipulate electron-transfer processes to optimize desired chemical and/or physical properties for many systems. Unfortunately, the actual electron-transfer process is often difficult to study directly, especially in those oxidation reduction reactions where the electron transfer is one in a series of rapidly occurring steps. Electron transfer in mixed-valence compounds is a simpler process whose understanding can provide fundamental information which relates to a wide range of electron-transfer phenomena.

Experiments aimed at determining electron-transfer rates in a variety of mixed-valence compounds have been undertaken by using physical methods which include electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), magnetic

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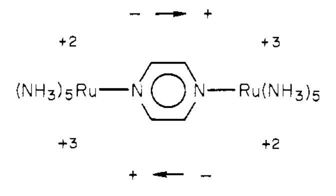
susceptibility, Mössbauer spectroscopy, electron spectroscopy for chemical analysis (ESCA), infrared spectroscopy (IR), Raman spectroscopy, ultraviolet–visible spectroscopy (UV–vis), and X-ray crystallography. The shortcomings of these techniques are perhaps best illustrated by the data which has been obtained for the dimeric system (μ-pyrazine)bis(pentaamineruthenium)(5+) tosylate.[1]

For this dimer, the experimental conditions appropriate for observing the electron transfer as a dynamic process have not been found. The odd electron in the molecule appears to be either completely localized or completely delocalized on the time scale of all of the experiments which have been carried out to date. The electron transfer looks slow on the time scales of the ESCA, Raman, Mössbauer, and EPR experiments and fast on the time scale of the NMR experiment though significant variation in the phase often accompanies use of the different methods. These experiments bracket the electron-transfer rate to between $k \geq 10^6$ Hz and delocalized. The actual rate of the transfer is still unknown as is the energy of activation for the transfer. Variable-temperature studies that have been atttempted are unrevealing due to relaxation problems associated with the d^5 ruthenium metal centers which mask line width effects attributable to a dynamic electron-transfer process. The Mössbauer results also suffer from poor resolution due to a large recoil fraction contribution to the data even at 4.2 K.

The above list of experimental difficulties is by no means complete but serves to demonstrate that new techniques are needed if mixed-valence compounds are to be studied in the detail that they deserve. Minimum requirements for such techniques are (1) the ability to operate over a wide range of frequencies, especially in the region from 10^6 to 10^{12} Hz where conventional techniques tend not to operate and where the apparent electron-transfer rates fall for a large number of mixed-valence compounds and (2) the ability to examine mixed-valence compounds whose electronic configurations or metal centers are not ideally suited for study by conventional spectroscopic techniques. Competing relaxation processes should be absent. Ideally, the technique should also be capable of examining mixed-valence compounds over a wide range of temperatures to allow studies which provide information concerning the energy and entropy of activation of the electron-transfer process, and how these thermodynamic quantities are influenced by outer-sphere effects.

One technique which can, in theory, meet the above requirements is called time domain reflectometry, TDR. This technique is used to determine the dielectric relaxation properties of both solid and liquid samples over a wide range of temperatures and frequencies. The physical property examined in this technique is common to all mixed-valence compounds independent of what the metal centers are or what electronic configurations are involved. That property is the change in the direction of the dipole moments in the sample which accompanies any electron transfer of this type.



By determining the rate at which these dipole moments are oscillating, one can determine the rate of intervalence electron transfer. The purpose of this investigation is to see if the techniques of time domain reflectometry can indeed be used to provide useful information concerning rates of intervalence electron transfer in a mixed-valence compound. The compound chosen[3] for detailed study was europium sulfide, Eu_3S_4, since it is one of the few mixed-valence systems studied to date which shows definitive dynamic electron-transfer effects in Mössbauer data.[2] In this study both Mössbauer and TDR data were taken over a wide temperature range for the same europium sulfide sample and compared.

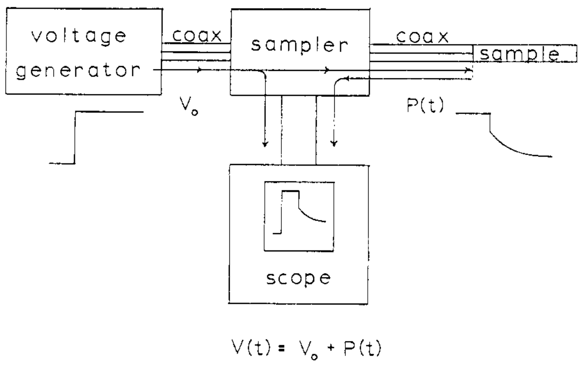


Figure 1. The basic components of the TDR apparatus. A tunnel diode pulse generator produces a square-wave voltage pulse, V_0, which is propagated down a section of coaxial cable to a sampling system. this sampler detects the pulse and displays it on an oscilloscope. The pulse is propagated through the sampler and down another section of coaxial cable until it encounters the sample cell, which is a section of coaxial cable which terminates the line. Components of the voltage pulse reflected from the sample cell back to the sampler are displayed on the oscilloscope superimposed on the signal due to the initial pulse V_0. The direct reflectance technique is shown on the scope.

Theoretical Background

A. Dielectric Relaxation. The theory of dielectric relaxation has been developed elsewhere[4] and, accordingly, only a brief outline of the theory relative to TDR will be given. When a dielectric material is placed in an electric field, there is a tendency for the dipole moments in the material to align themselves with the field. The field induced polarization creates an internal field opposing the applied field. The dielectric constant, ϵ, measured is the ratio of the applied field to the created effective field.

Time domain reflectometry measures the dielectric relaxation properties of a sample by monitoring the change in the dielectric constant, ϵ, as a function of time after the application of an electric field pulse. For a typical Debye dielectric, this change can be described by

$$\epsilon(t) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)(1 - e^{-t/\tau}) \qquad (1)$$

When the electric field is applied, the sample is immediately polarized to give a dielectric constant corresponding to ϵ_∞, the optical or high-frequency dielectric constant. From this initial value, the dielectric constant continues to increase, exponentially approaching the value of ϵ_0, the static dielectric constant, as any dipoles which exist in the sample have a chance to orient themselves with the applied field. The dielectric relaxation time, τ, is a measure of the rate at which the dipoles in the system can move to achieve this preferred orientation.

Until about 10 years ago most dielectric relaxation data were collected by using point-by-point fixed-frequency measurements. These measurements are time consuming, difficult to carry out, and usually cover narrow frequency ranges, especially in the high-frequency microwave region. These restrictions limit the number of high-frequency dielectric relaxation studies which have been reported. Since then new time domain methods[5-8] have been

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(2) Berkooz, O.; Malamud, M.; Strikman, S. *Solid State Commun.* **1968**, *6*, 185.

(3) Bunker, B. C.; Kroeger, M. K.; Richman, R. M.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 4254.

(4) (a) Prock, A.; McConkey, G. "Topics in Chemical Physics", Elsevier: New York, 1962. (b) Kauzmann, W. *Rev. Mod. Phys.* **1942**, *14*, 12. (c) Cole, R. H. *Annu. Rev. Phys. Chem.* **1977**, *28*, 283. (d) Smyth, C. P. *Ibid.* **1966**, *17*, 433.

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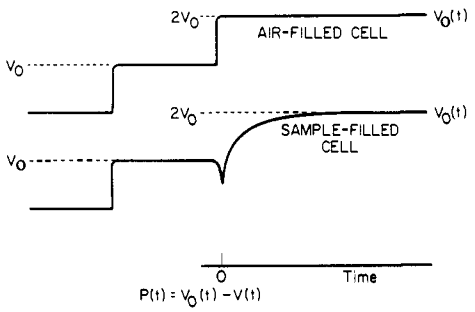

Figure 2. The comparison between the reference (air-filled) and the sample cells which determines $P(t)$, the total reflection coefficient. The voltage pulse encounters the sample surface at time zero. The total reflection coefficient, $P(t)$, of eq 2 is the difference between the two curves shown.

developed which are relatively easy to use and can provide broad-band frequency information on a sample from a Fourier transform analysis of the dielectric response of the sample to a step voltage.

B. Time Domain Reflectometry. The block diagram in Figure 1 illustrates the basic experimental apparatus used. In this apparatus, the dielectric sample to be studied is contained in a section of coaxial cable, which serves the function of the parallel plate capacitor in the preceding discussion. The sample is subjected to the electric field produced by a voltage pulse which is generated at one end of the apparatus. Analysis of this voltage pulse before and after it encounters the sample forms the basis for the time domain reflectometry techniques.

After leaving the voltage generator, the voltage pulse is propagated down a section of coaxial cable to the sampling gate or detector. The pulse, V_0, is detected as it goes through the detector and is displayed on an oscilloscope. It then continues down another section of coaxial cable until it encounters the surface of the dielectric sample. The sample has different propagation characteristics than empty coaxial cable and represents an impedence mismatch in the coaxial line. The incoming voltage pulse is partially reflected and partially transmitted. Many such reflections occur at both the front and back surfaces of the sample. All reflected components of the voltage pulse which are propagated back to the detector are displayed on the oscilloscope superimposed on the signal due to the incident V_0. The voltage response as a function of time appears on the screen as

$$V(t) = V_0 - P(t) \tag{2}$$

where V_0 is the response of an air-filled cell and $P(t)$, the total reflection coefficient, is the difference between V_0 and the observed voltage response. The resulting pulse display is illustrated in Figure 2. The appearance of $V(t)$ depends on the thickness of the sample, the way in which the coaxial cable containing the sample is terminated, the time scale of the observation, and the relaxation characteristics of the sample.

The upper frequency limit for determining the dielectric response of a sample arises because the TDR voltage pulse has a finite rise time of around 40 ps. It is impossible to resolve relaxation events which occur within this rise time. Inverting the rise time sets the upper frequency limit at about 2.5×10^{10} Hz. The upper frequency limit is further lowered to about 10^{10} Hz due to the small Fourier component of the incident pulse. The multiple reflectance TDR techniques rely on an analysis of all of the reflections which return to the sampler. These techniques have a maximum time window of around 10^{-6} s leading to a lower frequency limit of around 10^6 Hz due to the nonideal low-frequency impedence characteristics of the coaxial lines used. Therefore, the effective frequency range of the multiple reflectance TDR techniques is from around 10^6 Hz up to around 10^{10} Hz. It is significant that this frequency range effectively spans most of the gap not covered by the more conventional techniques mentioned earlier. Of the various multiple reflection techniques reported,[5-8] the sample termination technique[8] was selected for use in this study for ease in filling the sample cell.

In the multiple reflectance TDR techniques, the total reflection coefficient $P(t)$ is the infinite sum of all of the reflections returning to the detector. Equations have been derived[8] which allow the dielectric constant of the sample to be determined as a function of either time or frequency. Unfortunately, the equations in either domain cannot be solved analytically and are solved numerically. For this study, the analysis developed by Cole[8] has been employed. His method involves using a Taylor series expansion of the voltage propagation equations which describe $P(t)$. The series is truncated after terms which are second order in the sample thickness d. This truncation is valid for relatively thin samples as will be discussed later. His equation for the sample termination method is

$$\Phi(t) = \epsilon(t - \tfrac{1}{2}T_r) + \frac{C_s}{dC_c} = \frac{c}{d}\int_0^t \frac{p(t')}{2V_0}\mathrm{d}t' + \frac{c}{d}\int_0^t \frac{p(t')P(t-t')}{4V_0^2}\mathrm{d}t' + \frac{c}{d}\,\frac{T_rP(T_r)P(t)}{8V_0^2} \tag{3}$$

where $\Phi(t)$ is the response function which ideally approximates $\epsilon(t)$, T_r is the rise time of the voltage pulse (about 40 ps), C_s is stray end capacitance, C_c is coaxial line capacitance per unit length, d is the length of the sample-filled section of the line, c is the speed of light, and $P(t)$ is given by eq 2. C_s is usually so small that the term C_s/dC_c can be neglected. (This term has no influence on relaxation time.) If C_s is assumed to be negligible and the sample length is correctly obtained, then $\Phi(t \rightarrow 0)$ is ϵ_∞ and $\Phi(t \rightarrow \infty)$ is ϵ_0.

The relaxation time, τ, is readily determined from $\Phi(t)$ by using Guggenheim's method of plotting logarithms of differences in Φ as a function of t.

$$\Delta\Phi(t) = \Phi(t + n\Delta) - \Phi(t) \tag{4}$$

The constant time interval $n\Delta$ is selected randomly. If a single relaxation time describes the dielectric response function, the resulting Guggenheim plot ($\ln(\Delta\Phi(t))$ vs. t) should give a straight line having a slope of $-1/\tau$.

In using a series approximation scheme such as Cole's, it is important to determine whether the approximation is sufficiently close to the true propagation equations to give accurate relaxation times. For the Cole method, the validity of the approximation can be checked in several ways. One effective way to check if the method is providing accurate relaxation times is to see if changing the sample thickness, d, changes the value calculated for the relaxation time. If the relaxation time calculated is independent of the sample thickness, then the sample thickness can be assumed to be thin enough to make the approximation valid. If the relaxation time varies with sample thickness, then this means that the sample is too thick to describe that particular relaxation process adequately. If the sample is relatively thin and if the relaxation time apparent in the TDR data is near the TDR rise time, this means that the relaxation process is fast on the TDR time scale.

Experimental Section

Europium sulfide, Eu_3S_4, was prepared by the standard technique[2] of heating stoichiometric amounts of EuS (ROC/RIC) and sulfur in a sealed evacuated quartz tube at 600 °C for 4 days. The results obtained by elemental analysis indicate a stoichiometry for the final product between Eu_3S_4 and Eu_4S_5.

The TDR instrumentation used in these experiments consisted of the following components, all of which were purchased from Hewlett-Packard Co.: 1815B TDR/Sampler, 182C Oscilloscope, 1817A Sampler, 1106B Tunnel Diode Mount, 7045A X-Y Recorder, and three 20-cm long sections of precision coaxial cable equipped with APC-7 connectors (air line extension 11567A). These components were interconnected as described in the literature.[6] Two sections of the 20-cm coaxial cable were placed between the tunnel diode mount and the detector, and the other was positioned between the detector and sample cell. This configuration was used to move the unwanted reflections[6] which result in the impedence mismatches between the 50 Ω coaxial lines and the 55 Ω sampling system to positions where they would cause the least interference in the TDR trace.

The sample cell used consisted of one 10-cm section of precision coaxial cable with APC-7 connectors (air line extension 11566, Hewlett-

Table I. TDR Results for Eu_3S_4

T, K	τ,[a] ps	τ,[b] ps
339	208 (8)	416
319	277 (14)	554
296	503 (10)	1006
283	774 (22)	1548
259	1173 (27)	2346

[a] These data were fit to the equation $\tau = \tau_0 e^{E_{th}/RT}$ with τ_0 = 0.476 ps and E_{th} = 0.177 eV. [b] Corrected to correspond to Mössbauer times.

Packard). A similar section of cable was used to generate empty cell reference data used in conjunction with the multiple reflectance methods. The cell was opened for filling by removing the APC-7 connector from one end of the cell and unscrewing the pin connecting the coaxial bead which seals that end of the coaxial cable to the inner conductor of the coaxial line. After removal of the bead, the pin was replaced to keep the sample out of the pin cavity during the filling procedures.

Solid samples were introduced into the TDR sample cell as fine powders. These powders were packed into the cell by tapping small amounts of powder. The sample thicknesses, d, could be determined directly for the solids by measuring the difference in length of glass tubing inserted into the packed and empty cell with calipers. This method gives sample thicknesses to an accuracy of ±0.02 cm, resulting in an error of less than 10% in the determination of d for most samples.

The use of packed powders in the TDR cell can give rise to three potential problems. First, since the space occupied by the sample is partially occupied by air, the values obtained for the dielectric constant will be lower than the true dielectric constant of the sample. One can crudely correct for this by multiplying $\Phi(t)$ by the ratio of densities of the solid and packed powder. Second, the air space in the sample influences its thermal conductivity, making it difficult to monitor and control the sample temperature. The third potential problem can be present if the powder exhibits significant conductivity, as is the case for many of the extended lattice mixed-valence systems. These samples can exhibit interfacial polarization effects[9] which can give rise to dielectric relaxation, even if there is no relaxation process present in the bulk solid. Fortunately, these polarization effects have relaxation times which are rarely shorter than 10^{-6} s and should therefore not give rise to any relaxation effects on the TDR time scale.

Reference data $V_0(t)$ were obtained by using an empty sample cell. TDR curves representing $V_0(t)$ and $V(t)$ were generated on the same X-Y recording and time referenced to one another as described by van Gemert.[6] A computer program was written to analyze the data using eq 2–4.

The sample temperature was controlled by immersing the sample cell in a constant-temperature bath. The cell was isolated from the bath by using a glass test tube to prevent the slush bath from coming into contact with the exposed connectors. Such contact resulted in anomalous effects in the TDR spectrum. The sample was immersed in the slush bath for at least 30 min to allow the sample to equilibrate. The temperature of the sample in the cell was calibrated to the outside bath temperature by initially placing a thermocouple in the sample.

Mössbauer spectra were obtained on the Mössbauer apparatus built and operated by Dr. P. G. DeBrunner of the Materials Research Laboratory for the University of Illinois in Champaign. The γ-ray source used for the europium Mössbauer experiments was $^{151}SmF_3$. All of the spectra shown here were obtained by Steve Suib working in conjunction with R. M. Emberson and Dr. DeBrunner.

Results and Discussion

TDR spectra were obtained on the TDR apparatus described previously. The dielectric response functions were obtained numerically from eq 3 for each temperature. Guggenheim's method was used to obtain the relaxation times for the corresponding temperatures. The relaxation times obtained are shown in Table I.

At room temperature, the mixed-valence Eu_3S_4 sample exhibits clear dielectric relaxation behavior in its multiple reflectance (sample termination) TDR spectrum. Since this relaxation is not seen for the parent compound EuS, the reasonable explanation for this rapid relaxation process is to attribute it to an intervalence electron-transfer process. Spectra for both Eu_3S_4 and EuS are presented in Figure 3. The relaxation time associated with the TDR trace changes as a function of temperature as shown in Figure 4 with lower temperatures leading to longer relaxation times. This type of behavior is expected if there is a finite energy barrier to the electron-transfer process.

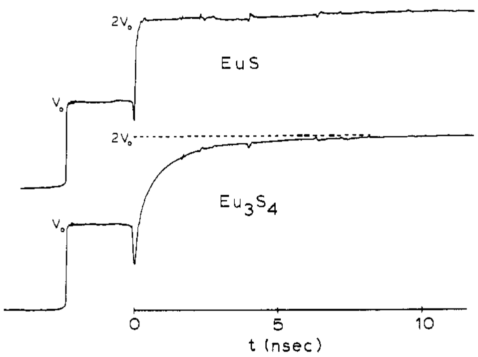

Figure 3. Multiple reflectance TDR for europium sulfides. The upper trace is that generated in the TDR for the compound EuS. No dielectric relaxation is observed for this sample. The lower trace is obtained for a mixed-valence europium sulfide having the stoichiometry of Eu_4S_5. Pronounced dielectric relaxation is observed for this sample at room temperature, as evidenced by the expotential curve which approaches a value of $2V_0$ at long times.

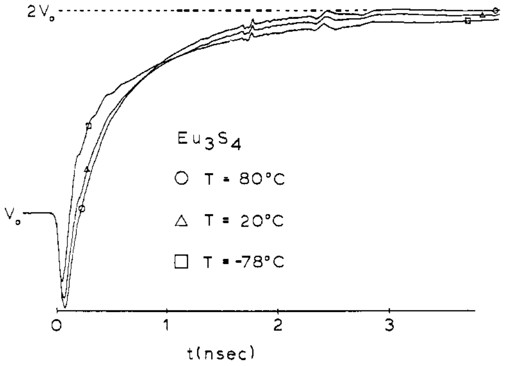

Figure 4. The temperature dependence of the TDR trace.

The data give good fits to straight lines in the Guggenheim plots at all temperatures which is indicative of a single exponential relaxation process. Deviations from this line which occur at times which are less than 100 ps are apparently caused by rise time effects and the result of truncating the series expansion in eq 3. The relaxation times calculated from the slopes of these lines are unaffected by the value of $n\Delta$. The relaxation times obtained at a given temperature for a variety of sample thicknesses and values of $n\Delta$ were found to agree within about 10%, which is roughly the level of uncertainty in the determination of the sample thickness, d.

The relaxation times associated with the electron-transfer process vary from 208 (8) ps at 339 K to 1173 (27) ps at 259 K. An Arrhenius plot shows that the data give a reasonable fit to a straight line (R^2 = 0.980) whose slope leads to the thermal energy barrier to the electron transfer. The value obtained is 0.18 eV or 1430 cm^{-1}. If the TDR data are expressed in the form of the equation $\tau = \tau_0 e^{E/kT}$, then the value of the preexponential factor τ_0 is calculated to be equal to 0.5 ps. These variable-temperature results also show that the concentration of charge carriers in the sample is constant, since the maximum value of ~25 obseved for $\Phi(t)$ remains constant with temperature. (If the appropriate density corrections are made, this dielectric value corresponds to ϵ_0.) An estimate for ϵ_∞ produces a value of around 7.

The relaxation times obtained by using the above analysis are dielectric relaxation times. These relaxation times are macroscopic relaxation times which differ from molecular times because of "internal field" effects. Although this affects the true values, it has little or no effect upon the activation energy. The actual rates

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[9] Miles, P. A.; Westphal, W. B.; von Hippel, A. *Rev. Mod. Phys.* **1957**, *29*, 279.

Table II. Mössbauer Results for Eu_3S_4

T, K	$1/\tau$,[a] s^{-1}	τ,[b] ps
393	5.62 (30) × 10^9	178
350	2.06 (01) × 10^9	485
300	9.90 (02) × 10^8	1010
285	2.02 (01) × 10^8	4951
270	1.05 (01) × 10^8	9524
230	5.06 (24) × 10^6	1.98 × 10^6
220	127 (3200)	7.87 × 10^9
90	1.61 (453) × 10^{-4}[b]	6.21 × 10^{15}[b]

[a] These data were fit to the equation $\tau = \tau_0 e^{E_{th}/RT}$ with τ_0 = 0.054 ps and E_{th} = 0.267 eV. [b] This value was not used in the determination of the thermal barrier.

of the electron transfer can be calculated from these relaxation times by using the relationship

$$k = 1/2\tau \tag{5}$$

For solid mixed-valence compounds the "dipole motion" corresponds to an intervalence electron transfer between a pair of metal sites:

$$M_1^{Z+}—M_2^{(Z+1)+} \rightarrow M_1^{(Z+1)}—M_2^{Z+} \tag{6}$$

Here, one electron transfer changes the population difference of the two states by two. Commonly, relaxation times obtained by Mössbauer spectroscopy and other techniques are assumed to be equal to $1/k$, so in order to compare TDR relaxation times to relaxation times obtained by other methods, one should divide the value of the dielectric relaxation time by a factor of 2.

Mössbauer results for the same sample of Eu_3S_4 used in the TDR experiments lead to different values for both the energy barrier to the electron transfer and τ_0. Mössbauer spectra were obtained at eight temperatures ranging from 90 K up to 393 K. Some of these spectra are reproduced in Figure 5. In order to make a direct comparison between the result reported by Berkooz[2] for Eu_3S_4 and the results obtained on the sample studied here, the spectra in Figure 5 were analyzed by using the line-shape equations developed by Wickman[10] which were used in the Berkooz analysis. A listing of the parameters obtained by simulating the spectra appears in Table II.

The Eu_3S_4 sample studied here is slightly different from the sample studied by Berkooz. A small peak is evident in the spectra at temperatures above the coalescence temperature which indicates that the sample contains roughly 4% of an Eu(III) impurity which is not participating in the electron transfer. The isomer shift for this impurity is 1–2.5 mm/s. The Mössbauer results yield a thermal barrier to electron transfer of 0.267 eV (2153 cm^{-1}) which is in agreement with Berkooz's value of 0.24 eV. However, there is obvious disagreement between the TDR and Mössbauer results.

Conductivity studies[11,12] lead to an activation energy for conduction of 0.163 eV in the temperature region employed in the TDR and Mössbauer studies. The mechanism responsible for conduction, electron hopping among the mixed-valent europium sites, is assumed to be the same mechanism responsible for intervalence transfer.[2,11,12]

A phase transformation occurs in the sulfide at about 168 K which is characterized by a sharp break in the resistivity and thermal emf of the sample. This phase transformation is thought to be due to charge ordering which produces tetragonal symmetry in the unit cell. Below the transition temperature the activation energy is 0.21 eV.

Of the Mössbauer and TDR studies performed above the phase transformation temperature, the TDR results are in excellent agreement with the conductivity results. An explanation is needed for the discrepency with Mössbauer relaxation times. The discrepency is most likely caused by the assumptions inherent in the Mössbauer analysis. The line-shape analysis employed[2,10] requires that the natural line widths of Eu(II) and Eu(III) be the same and that the shifts are known at all temperatures to a high degree of accuracy. This is difficult to determine when the two peaks are near coalescence. Obviously, some questionable assumptions about the linewidths and shifts must be made. For example, in the Berkooz analysis, and ours, it was assumed that the isomer shifts and line widths observed at low temperatures in the slow-exchange limit are temperature independent. It was also assumed that both Eu(II) and Eu(III) have the same natural line width at all temperatures and the same recoil free fraction of γ-rays, giving rise to the intensity of the signal over the entire temperature range. Finally, it was assumed that the lifetime of the mobile electrons is identical at all sites in the lattice and that the electron wave functions are localized on a single europium center at any given instant in time. The spectra were corrected for the second-order Doppler shift. Thus large errors are possible in the Mössbauer relaxation times. This is because τ is obtained only after simulation of isomer shifts and line widths which exist independently of dielectric relaxation (remember, dielectric relaxation broadens Mössbauer spectra, whereas there would be no TDR signal at all with the intervalence transfer in Eu_3S_4—a much more straightforward analysis is thus possible). Due to errors in the isomer shifts, only Mössbauer relaxation times which are the same order of magnitude as the lifetime of the excited state of ^{151}Eu, 1600 ps are meaningful. Even those relaxation times are only accurate to around an order of magnitude. The TDR results, which are in very good agreement with the conductivity studies, appear to provide a more accurate measure of this quantity than Mössbauer.

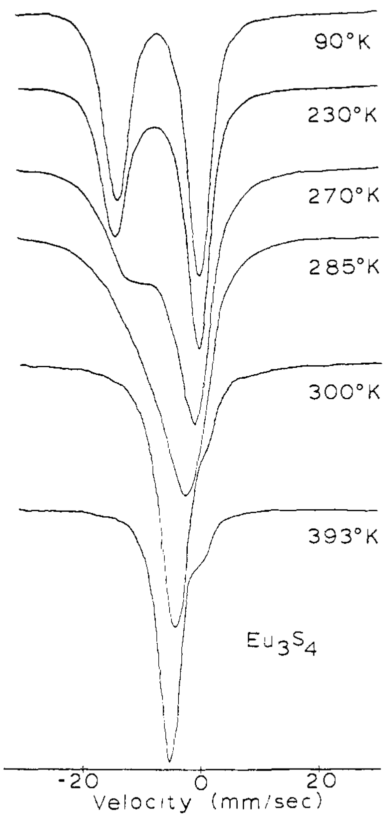

Figure 5. Variable-temperature Mössbauer spectra for Eu_3S_4. Isomer shifts are measured relative to $^{151}SmF_3$. The observed behavior is indicative of an electron-transfer process which is occurring on the Mössbauer time scale. An anomalous peak in the high-temperature spectra having about 5% of the total spectral intensity is caused by a Eu(III) species which is not taking part in the electron exchange.

Allen and co-workers have reported[13] the diffuse reflectance spectrum of Eu_3S_4 which contains two absorption bands at 8770

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and 21 370 cm^{-1} with continuous absorption commencing at about 21 000 cm^{-1}. The band at 21370 cm^{-1} has been attributed to an f → d Eu(II) transition. The band at 8770 cm^{-1} has been attributed to intervalence transfer between Eu(II) and Eu(III). Assuming Hush theory[14] to apply to Eu_3S_4, then the intervalence transfer band should be related to the half-width at half-height of the band ($E_{1/2}$) by

$$E_{1/2} = \sqrt{16[\ln (2kt)]E_{\rm iT}} \qquad (7)$$

For the intervalence transfer band at 8770 cm^{-1} the half-width at half-height should be 4500 cm^{-1}. It is only 3500 cm^{-1}. The measured half-width at half-height implies that the intervalence transfer band should be centered at 5300 cm^{-1} and not at 8700 cm^{-1}. Obviously, Hush theory has broken down for Eu_3S_4. However, this is expected since Eu_3S_4 is a strongly interacting, class II mixed-valence compound and Hush theory was developed for weakly interacting sites.

The thermal barrier and the intervalence transfer band are also related by Hush theory:

$$E_{\rm th} = \tfrac{1}{4}E_{\rm iT} \qquad (8)$$

Thus, the thermal barrier obtained from the Mössbauer simulations predicts $E_{\rm iT}$ = 8612 cm^{-1} in excellent agreement with the experimental value. This agreement is fortuitous because we have just concluded from eq 7 that Hush theory does not apply (Eu_3S_4 is a class II compound on the basis of the half-width at half-height for the IT band. Vibronic coupling should lower the thermal barrier yielding a prediction of $E_{\rm IT}$ which is too low. This supports our conclusion that the Mössbauer result is incorrect. The thermal barrier obtained by TDR predicts $E_{\rm iT}$ = 5716 cm^{-1}, and this is the kind of miss expected when Hush theory is used on a class II system.

Finally, using Debye's development of dielectric theory[4] the permanent dipole moment of the sample may be obtained from[15]

$$M = \sqrt{(\epsilon_0 - \epsilon_\infty)3kT/4TN} \qquad (9))$$

where N is the unit concentration. Assuming a density correction factor for the TDR data of 2, a value of about 7 × 10^{-18} esu is obtained at room temperature. The polarizability may be estimated from

$$L = \frac{M^2}{3kT} = \frac{\epsilon_0 - \epsilon_\infty}{4TN} \qquad (10)$$

from which a value of 4 × 10^{-22} cm^3/molecule is obtained. Equations 9 and 10 are crude approximations, but they show that Eu_3S_4 has a very large dipole moment as is expected from the large distance between the charges in this extended lattice.

Conclusions

The use of time domain reflectrometry as a tool to obtain rates of intervalence transfer has been demonstrated. The TDR results have been compared to Mössbauer results obtained from the same sample and have been found to be more accurate. The breakdown of Hush theory applied to this class II sample has also been noted. This article represents the first reported use of TDR to obtain relxation times for intervalence transfer in a mixed-valence species and to determine from those times the thermal barrier for electron transfer. The viability of TDR for the extraction of accurate relaxation times is very significant because reliable values for the relaxation times of mixed-valence species are critical for the theoretical development of models to describe the process of intervalence transfer in diverse systems. Barriers will often be small and differences smaller. Clearly, TDR has the potential to play a significant role in the experimental determination of relaxation times.

Registry No. Eu_3S_4, 12345-98-1; EuS, 12020-65-4; Eu_4S_5, 82190-34-9.

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(15) Since a microscopic field is being used, Onsager's equation should be used instead of the Debye equation. However, for qualitative purposes the mathematically more simple Debye equation should be sufficient.

Syntheses, Kinetics, and Mechanism of Formation of Polynuclear Hydroxo-Bridged Complexes of (*trans*-1,2-Diaminocyclohexane)platinum(II)

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Abstract: The synthesis and ^{195}Pt chemical shifts of the hydroxo-bridged dimer and trimer, isolated from an aquated solution of bis(nitrato)(*trans*-1,2-diaminocyclohexane)platinum (I), at different pH are described. The chemical shifts of these three complexes are widely separated, and ^{195}Pt NMR provides a convenient method for the investigation of dimer formation kinetics from I. Rate constants for the dimerization reaction calculated at different pD, temperature, and concentration agree well with the hypothesis that dimerization occurs with a rate-limiting bimolecular reaction of an intermediate hydroxo species formed by the loss of a proton from the parent complex.

The discovery of cisplatin[1] as an anticancer agent marks the beginning of the upsurge of interest in the use of metal complexes in cancer chemotherapy. The drug has found wide application in the treatment of a variety of cancers.[2] The continuing interest and stimulation has been triggered and guided by two objectives: first, to develop new metal complexes having superior spectra of activities, lower toxicities, better therapeutic indices, and higher solubilities than the presently existing drugs; and second, to un-

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