Reinvestigation of the Iron-57 Mössbauer Effect at High Pressures in Some Iron(II) Bis(phenanthroline) Complexes

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Some inconsistencies in the results of earlier high-pressure Mössbauer spectroscopic measurements on $Fe(o\text{-phen})_2(X)_2$ with $X = NCSe^-$, NCS^-, and N_3^- made it necessary to reinvestigate these complexes. The ^{57}Fe Mössbauer effect has been studied in detail between 0.001 and 45 kbar at room temperature. It has been found that a large part of the high-spin to low-spin transitions of the compounds with $X = NCSe^-$, NCS^-, and N_3^- abruptly occur near 9, 13.5, and 24 kbar, respectively. The present report supports a recent IR study although there is a discrepancy in transition pressures.

Introduction

It is well-known that the spin configuration of certain transition-metal complexes can be changed by temperature or pressure. One of the best known examples is $Fe(phen)_2$-$(NCS)_2$ (phen = 1,10-phenanthroline). Its well-documented abrupt spin crossover $^1A_1 \rightleftharpoons {}^5T_2$ has previously been extensively studied by Mössbauer spectroscopy,[1,2] IR spectroscopy,[1,3,4] and magnetic susceptibility measurements[1] as a function of temperature (for review see ref 5). It was demonstrated on the basis of heat capacity measurements by Sorai et al.[6] that the $^1A_1 \rightleftharpoons {}^5T_2$ transition is associated with a phase change of first order. Although the spin transition has been well established, the correlation between the results from various techniques has not been very satisfactory. In particular, a most recent high-pressure far-IR study by Adams et al.[7] established a complete spin transformation that takes place in the pressure region between 8 and 14 kbar. This conflicts with the classical Mössbauer high-pressure experiment by Fisher and Drickamer,[8] which suggested that increase of pressure induces a steady conversion of the high-spin to the low-spin state up to about 20 kbar, but only a partial conversion of about 80%. At higher pressure a decrease in the amount of low-spin and a partial reversion to high-spin behavior was observed. It was suggested[7] that the differences between the results of the different high-pressure experiments arise because of the type of high-pressure cell used by Fisher and Drickamer[8] applies far from hydrostatic pressure. Similar results were obtained by the authors for the Fe(II) complexes with $X = NCSe^-$ and N_3^-.[8] This calls into question details of the high-pressure work on the spin-crossover phenomenon by Drickamer. In the following we present a reinvestigation of the ^{57}Fe Mössbauer effect in the title complexes up to 45 kbar.

Experimental Section

Chemical Preparation. The iron(II) bis(phenanthroline) complexes were synthesized from iron enriched to 50 or 95% in ^{57}Fe, by using techniques from literature.[1,2] $Fe(phen)_2(NCS)_2$ was prepared by extracting a phenanthroline group from $(Fe(phen)_3)(NCS)_2 \cdot H_2O$ in a Soxhlet apparatus with use of acetone. The extraction was carried out over a period of about 2 weeks under a nitrogen atmosphere. $(Fe(phen)_3)(NCS)_2 \cdot H_2O$ was prepared by adding a saturated aqueous solution of potassium thiocyanate to a well-stirred aqueous solution of ^{57}Fe-enriched iron(II) ammonium sulfate and 1,10-phenanthroline hydrate.

$Fe(phen)_2(NCSe)_2$ and $Fe(phen)_2(N_3)_2$ were also prepared according to this method. Analyses for C, N, H, and unenriched Fe showed agreement within 0.2% of the calculated values.

High-Pressure Cell. High-pressure Mössbauer experiments were performed at room temperature up to 45 kbar by using a cell similar to that used in the pressure laboratory of G. M. Kalvius in München and described by Klein[9] so that details should not be reviewed here. In summary, the high-pressure device used in our experiment consists

of a clamp that contains the pressure cell. The body of the clamp is pressure loaded by using a commercial hydraulic press. The force acting on the cell is measured and stored by tightening a backing screw. Sintered boron carbide anvils (Elektroschmelzwerke Kempten) have been used in the present device. The absorber samples, kept between anvils, were embedded in UHU plus or in talc powder, which have good homogeneity in transmitting pressure. The γ-rays passing through the anvils are parallel to the direction of the applied force. The pressure approximately proportional to the acting force on the cell was calibrated with the known changes of the electrical conductivity of Bi and Tl. From the width of the corresponding transition curves we estimated a pressure gradient of about 1 kbar over the effective sample area.

Mössbauer Spectra. Mössbauer spectra were recorded in transmission geometry. The spectra were measured with a constant-acceleration spectrometer operating in the multiscaler mode. As detector a Xe gas proportional counter and a 40-mCi source of ^{57}Co in rhodium were used. The calibration was effected with a metallic-iron absorber. The utilization of a sample enriched to 50 or to 90% in ^{57}Fe allowed the relatively rapid accumulation of spectra. The typical count rate at the detector was 800 counts/s and about 3–5 days was required to accumulate each spectrum. All velocity scales and isomer shifts are referred to the Co(Rh) source at room temperature. To convert to the iron standard at 295 K, add +0.11 mm/s. All measurements were performed with the identical geometrical arrangement for source, absorber, and detector. The resulting data were carefully corrected for nonresonant background of the γ-rays and with respect to the small Fe contamination in the BC_4 anvils. Finally, the spectra were computer fitted to Lorentzian line shapes. The resulting parameters are accurate to about ±0.02 mm/s.

Results and Discussion

The results of magnetic susceptibility and Mössbauer-effect measurements reported in literature[5] for $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ are usually complicated by the fact that the transition of the high-spin to the low-spin species does not proceed to 100% of the $^1A_1$ state at very low temperature. However, our temperature-dependent Mössbauer-effect results show abrupt $^5T_2 \rightleftharpoons {}^1A_1$ transition for $X = NCS^-$ and $NCSe^-$ with decreasing temperature at 182 and 235 K, respectively. The low-temperature spectra demonstrate that our samples do not contain high-spin species at 4.2 K. Examples of ^{57}Fe spectra for $Fe(phen)_2(NCS)_2$ recorded at 4.2 and 296 K are

(1) König, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48.
(2) Ganguli, P.; Gütlich, P.; Müller, W. *J. Chem. Soc., Dalton Trans.* **1981**, 441.
(3) Takemoto, J. H.; Hutchinson, B. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 769. Takemoto, J. H.; Hutchinson, B. *Inorg. Chem.* **1973**, *12*, 705.
(4) Ferraro, J. R.; Takemoto, J. H. *Appl. Spectrosc.* **1974**, *28*, 66.
(5) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83–195.
(6) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555.
(7) Adams, D. M.; Long, G. J.; Williams, A. D. *Inorg. Chem.* **1982**, *21*, 1049.
(8) Fisher, D. C.; Drickamer, H. G. *J. Chem. Phys.* **1971**, *54*, 4825.
(9) Klein, U. F. Dissertation, Technische Universität München, 1976.

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Table I. Mössbauer Spectroscopy Results of Quadrupole Splitting ΔE_Q, Isomer Shift δ, and Area Fraction X for High-Spin (HS) and and Low-Spin (LS) Species at Various Pressures P

| compd	P, kbar	ΔE_Q(HS), mm/s	δ(HS), mm/s	X_{HS}	ΔE_Q(LS), mm/s	δ(LS), mm/s
Fe(phen)₂(NCS)₂	0.001	2.67	0.85	1.00		
	13.0	2.65	0.84	0.57	0.28	0.20
	14.0	2.62	0.84	0.20	0.28	0.20
	20.0	2.54	0.81	0.05	0.30	0.19
	40.0				0.35	0.16
Fe(phen)₂(NCSe)₂	0.001	2.51	0.86	0.96	0.28	0.22
	8.0	2.50	0.85	0.87	0.30	0.20
	10.0	2.48	0.84	0.11	0.32	0.20
Fe(phen)₂(N₃)₂	0.001	2.77	0.83	1.00		
	22.5	2.77	0.80	0.91	0.62	0.22
	23.0	2.74	0.79	0.65	0.63	0.21
	45.0	2.63	0.79	0.28	0.66	0.19
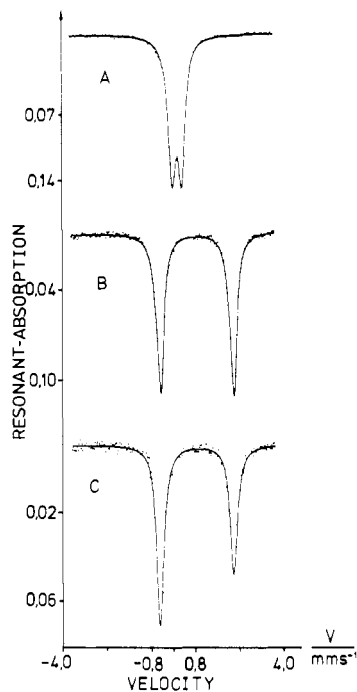
Figure 1. Mössbauer spectra of Fe(phen)₂(NCS)₂ at P = 0.001 kbar: (A) at 4.2 K; (B) at 296 K; (C) after releasing pressure at 296 K.

shown in Figure 1 (spectra A and B). These results are in agreement with the sample preparation "B" by Ganguli et al.,[2] who found that a high-spin residue depends to some extent on the preparation method employed. The authors showed that more rapid precipitation method will incorporate more imperfections into the crystallites than a slow extraction.

According to the Mössbauer-effect measurements as a function of temperature, Fe(phen)₂(N₃)₂ is not converted from the high- to the low-spin state by cooling.

Representative Mössbauer spectra of the samples with X = NCS⁻ and N₃⁻ are shown in Figures 2 and 3 as a function of high pressure up to 50 kbar, respectively. The values for the quadrupole splitting ΔE_Q, the isomer shift δ, and the area fraction X_{HS} are summarized in Table I. The velocity scale is calibrated against the used ^{57}Co(Rh) source at room temperature.

Fe(phen)₂(NCS)₂. At $P \leq 11$ kbar, the Mössbauer spectra consist of a single doublet characterized by the quadrupole splitting about ΔE_Q(HS) = 2.65 (2) mm/s with an isomer shift δ(HS) = 0.84(2) mm/s at 13 kbar. These values are characteristic of the high-spin ground state of Fe(II) ($^5T_2$). At P = 11 kbar, a slight asymmetry of the spectrum becomes apparent, which increases with increasing pressure. A second doublet becomes clearly visible at 13 kbar as origin of the asymmetry. The intensity of the second doublet, expressed
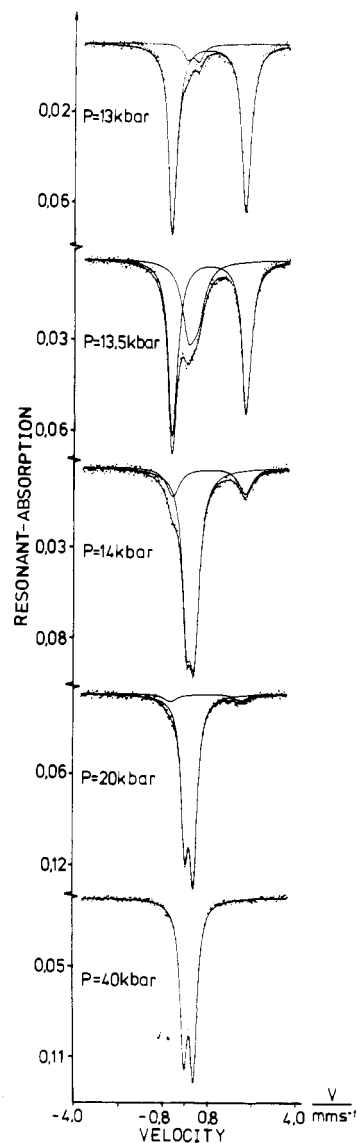
Figure 2. Mössbauer spectra of Fe(phen)₂(NCS)₂ at room temperature and at various pressures. The spectra demonstrate that a large part of the intensity of the iron(II) HS doublet (outer two lines) abruptly decreases in a rather narrow pressure region about 13.5 kbar.

by the area fraction, amounts at this pressure to about 8% of the total area of the spectrum. The Mössbauer parameters ΔE_Q(LS) and δ(LS) in Table I are typical of low-spin Fe(II) ($^1A_1$). With increasing pressure, a steady increase in the amount of low-spin ferrous species is observed. A large part of the spin transition from $^5T_2$ to the $^1A_1$ occurs in a rather narrow pressure region of about 13.5 kbar, where about 50%
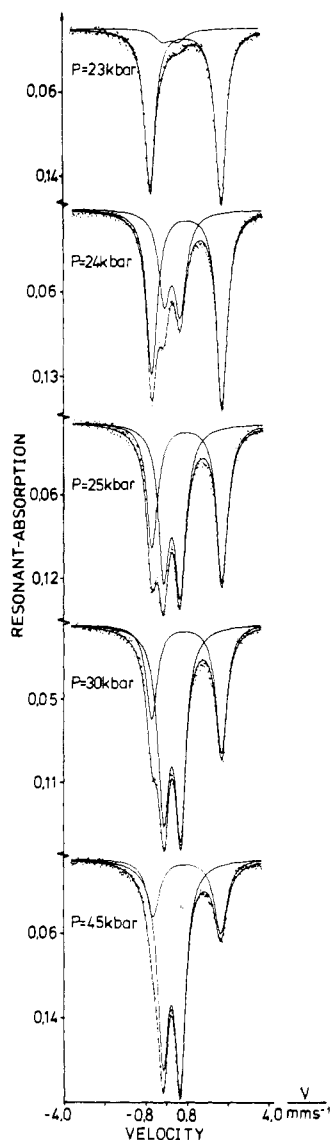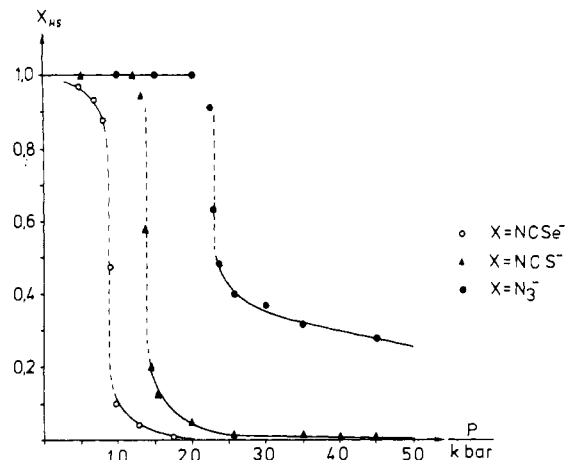
Figure 3. Mössbauer spectra of Fe(phen)₂(N₃)₂ at room temperature and various pressures. The spectra demonstrate that a large part of the intensity of the iron(II) HS doublet (outer two lines) abruptly decreases between 23 and 25 kbar and residual high-spin material is still present at about 45 kbar.

Figure 4. Area fraction X_{HS} of the iron(II) high-spin doublet from the Mössbauer spectra of Fe(phen)₂(X)₂ with X = NCS⁻, NCSe⁻, and N₃⁻ as a function of high pressures up to 45 kbar.

of the spin species have changed their spin state. The progress of the pressure-induced spin transition may be followed in terms of the high-spin content X_{HS} as a function of pressure P. The area fraction of the high-spin doublet of the spectra $X_{HS} = A(\text{HS})/(A(\text{HS}) + A(\text{LS}))$ is shown in Figure 4. This equality implies that the Debye–Waller factors of the high-spin and low-spin molecules are the same. Because of the fact that the mean-square amplitudes are different for those lattice modes that are associated with the electronic ground states ⁵T₂ and ¹A₁, the error may be estimated to be small. At higher pressure, an accurate determination of $\Delta E_Q(\text{HS})$ and $\delta(\text{HS})$ is not possible, the reason being the extremely low area fraction due to the ⁵T₂ ground state. At $P = 20$ kbar, $\Delta E_Q(\text{HS}) \simeq 2.54$ mm/s and $\delta(\text{HS}) \simeq 0.81$ mm/s may be considered as a reasonable estimate.

One can see from Figure 4 that the abrupt conversion of the high-spin content X_{HS} is followed by a lower rate of increase of conversion with pressure at $P > 14$ kbar. It is evident from the present studies that there is a complete conversion above 35 kbar for Fe(phen)₂(NCS)₂.

Fe(phen)₂(NCSe)₂. A similar complete transformation to the low-spin state is observed for this compound. As the pressure is increased above $P = 7$ kbar, the amount of high-

spin Fe(II) ions strongly decreases. From Figure 4 one can see that the spin transition ⁵T₂ ⇄ ¹A₁ abruptly occurs at about $P = 9$ kbar. The spectra from 20 to 45 kbar likewise represent fully transformed material suffering the usual progressive changes with pressure.

Fe(phen)₂(N₃)₂. As stated above a transformation to the low-spin form is not induced in this compound by cooling. However, one can see from Figures 3 and 4 that a large part of the high-spin amount changes the spin-state in a narrow pressure region at about 24 kbar. At the calibrated pressure of 25.5 kbar, major changes have occurred. This Mössbauer spectrum is consistent with a transformation of at least 63% of the sample to low spin. As in Figure 4, indicated residual high-spin material is still present and the increase of conversion rate is very low.

The results may be summarized as follows: Compared to the previous high-pressure experiments by Fisher and Drickamer[8] our results show a sharp spin transition ⁵T₂ ⇄ ¹A₁ for Fe(phen)₂(NCS)₂ and Fe(phen)₂(NCSe)₂ in a very narrow pressure range about $P_c \simeq 13.5$ and 9 kbar, and hence, practically no high-spin species are present above 30 and 20 kbar, respectively. The results up to 50 kbar did not establish the rather curious spin equilibria vs. pressure data,[8] which suggest that increase of pressure first brings about partial conversion of high-spin material to low-spin and that with further pressure increase there is partial reversion to high-spin behavior. Our results are in agreement with the most recent IR investigations under high pressure by Adams et al.,[7] although the reported critical pressure values are evidently lower than found in our experiment. A marked increase of the Mössbauer line widths of the low-spin molecules, presumably as a consequence of the small pressure gradient, occurs in the critical pressure regions. Neither an irregularity in the quadrupole splitting as seen in the temperature dependence[2] nor an anomaly in the behavior of the isomer shift as seen in the pressure dependence[8] could be observed.

One disturbing feature of the high pressure Mössbauer spectra studied, is the increasing asymmetry of the intensity of the absorption lines with pressure (Figures 2 and 3). After release of the pressure, spectra consist again of only one doublet having the same isomer shift and quadrupole splitting as in the unpressed case. However, by comparison of the spectra in the middle (spectrum B) and at the bottom (spectrum C) of Figure 1, it can easily be seen that the intensity ratio before and after applying pressure has drastically changed in magnitude. Probably, the main feature of asymmetry is due to the effect of partial orientation of crystallites and texture inside our transmitting substance. The compounds tend to pack with

preferential orientation with increasing pressure even when finely ground. After release of pressure and grinding, the effect of anisotropy has vanished.

As seen, $Fe(phen)_2(N_3)_2$ is not completely converted from high- to low-spin form with increase of pressure. It is necessary to know that the thermodynamic criterion for increase of conversion with pressure is that the volume of the system as a whole decreases with increasing conversion at constant pressure and temperature.[10] This may be realized by bond shortening or closer packing of the molecules due to changes in their electronic structure.

Single-crystal results of a related compound $Fe(dip)_2(NCS)_2$ reveal that the Fe–N(dip) bond length increases from about 2.17 Å in the $^5T_2$ ground state (293 K) to about 2.03 Å in the $^1A_1$ ground state (100 K). The difference of 0.14 Å clearly reflects the change in radius of the iron(II) ion in going from the high-spin $t_2^4 e^2$ to the low-spin t_2^6 configuration. The Fe–N(NCS) bond length shortens to about 0.08 Å.[11] In agreement with IR results,[12] there is no increasing of the N–C bond length of the NCS⁻ ligand on passing from the $^5T_2$ state to the $^1A_1$ state. In the absence of other structural data, one assumes a similar FeN bond shortening in the other studied $Fe(phen)_2(X)_2$ compounds. However, from the chemistry of coordinated azides it is quite apparent that the larger the π-donor interaction between the p orbitals on N (bound to the metal M) and the $d(\pi)$ orbitals on the metal M, the larger the difference between the two N–N distances. Another structural parameter of interest is the $M–N_\alpha–N_\beta$ bond angle, which varies between 117 and 132°,[13,14] in the expected range for the angle of a trigonally hybridized N_α atom. With increase of pressure the back-donation of the metal $d(\pi)$ electrons to the ligand π orbitals increases and may cause a strengthening of the structural effects above. Thus it may appear for $Fe(phen)_2(N_3)_2$ that steric factors and/or crystal

packing may influence the sharpness of the spin transition. In this connection it is interesting to know that the quadrupole splitting $\Delta E_Q(LS)$ in $Fe(phen)_2(N_3)$ is about 2 times greater than observed in $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ (Table I).

On the other hand, spectroscopic investigations on azido complexes place the azide ligand at the beginning of the spectrochemical series.[15] These ligands, which may act as π donors, have rather low f values, which are proportional to the ligand field parameter Δ and the covalent bonding. From the literature[15] we get the following sequence for the ratio of the different ligand field parameters: $\Delta(Cl^-):\Delta(N_3^-):\Delta(NCS^-):\Delta(CN^-) = 0.78:0.83:1.02:1.7$. From this, one expects that with decreasing f values the transformation is increasingly hindered, leaving a certain amount of high-spin residual. This trend seems to be observed by Fisher and Drickamer.[8] However, a related study on $Fe(phen)_2(X)_2$ with X = Cl, Br is currently under way in our laboratories.

In this connection, it is noteworthy that $Fe(phen)_2(CN)_2 \cdot H_2O$, which exhibits a very high degree of back-bonding to the empty cyanide ligand π^* levels, exists in the low-spin state at 0.001 kbar. Obviously, the dominant effect is the increase in the ligand field with pressure due to the increased back-bonding. The increase in the ligand field overcomes the spin-pairing energy and thus brings about the high-spin to low-spin transition.

Theoretical considerations on the problem of spin transitions as a function of pressure are in progress.

(10) Slichter, C. P.; Drickamer, H. G. *J. Chem. Phys.* **1972**, *56*, 2142.
(11) König, E. *Coord. Chem. Rev.* **1968**, *3*, 471.
(12) Baker, W. A.; Long, G. J. *Chem. Commun.* **1965**, *5*, 368.
(13) Dori, Z.; Ziolo, F. *Chem. Rev.* **1973**, *73*, 247.
(14) Müller, U. *Struct. Bonding (Berlin)* **1973**, *14*, 141.

(15) Williams, A. F. "Theoretical Approach to Inorganic Chemistry"; Springer Verlag: Berlin, 1979.

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Excited-State Properties of Lamellar Solids Derived from Hydrogen Uranyl Phosphate

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The excited-state properties of the layered compound hydrogen uranyl phosphate (HUP), $HUO_2PO_4 \cdot 4H_2O$, and of solids derived therefrom have been examined; the derivatives, prepared by intercalative ion-exchange reactions, have compositions based on stoichiometric proton substitution by NH_4^+, pyridinium, n-butylammonium, n-octylammonium, K^+, and Ag^+, 0.5 equiv of Ca^{2+} and Zn^{2+}, and 0.4 equiv of Cu^{2+}. These compounds have all been characterized by elemental analysis, IR spectroscopy, and X-ray powder diffraction; the last confirms the retention of the lamellar structure upon cationic substitution and reveals that the interlamellar spacing can vary considerably with the choice of cation. All of the samples exhibit electronic absorption spectra characteristic of the UO_2^{2+} chromophore. Except for the n-octylammonium, Ag^+ and Cu^{2+} salts, the samples all exhibit yellow-green emission characteristic of the UO_2^{2+} moiety when excited with blue or near-UV light at 295 K. Emission decay curves are exponential for all of the luminescent solids and yield lifetimes, τ, ranging from ~ 1 to 450 μs. HUP and its K^+, NH_4^+, pyridinium, and Ca^{2+} derivatives are all highly emissive with measured radiative quantum efficiencies, ϕ_r, approaching unity at 295 K. Values of τ and ϕ_r have been used to calculate radiative (k_r) and nonradiative (k_{nr}) rate constants for excited-state decay. Values of k_r are nearly constant at $\sim (1–2) \times 10^3$ s⁻¹ for the samples, whereas k_{nr} values span several orders of magnitude. Possible quenching mechanisms for the weakly emissive and nonemissive solids are described and compared with previously reported solution data.

The excited-state properties of inorganic solids are receiving considerable attention as a means of characterizing electronic structure and physical processes occurring within the solid. Useful applications of luminescence, traditionally the basis for such studies, have included the design of phosphors[1] and

light-emitting diodes,[2] as well as the characterization of semiconductor electrodes[3] and colloids.[4] Although numerous

(1) Leverenz, H. W. "An Introduction to Luminescence of Solids"; Dover: New York, 1968.