Electron-Spin-Resonance Spectrum of Divalent Europium in Thorium Dioxide*

M. M. ABRAHAM, C. B. FINCH,† R. W. REYNOLDS,‡ AND H. ZELDES§

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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Either 2-MeV electron or ^{60}Co γ irradiation was employed to reduce trivalent Eu in ThO_2 to the divalent state. The ESR spectrum of the Eu^{2+} ions could only be observed at temperatures below 77°K and posessed trigonal symmetry about the four $\langle 111 \rangle$ axes. The axial crystal field was so strong that only the $|M_J = \frac{1}{2}\rangle$ to $|M_J = -\frac{1}{2}\rangle$ transition was observed with a highly anisotropic g value ($g_{||} = 1.9678 \pm 0.0005$ and $g_\perp = 7.867 \pm 0.002$). Hyperfine structure was resolved but the angular variation was complex because of a nuclear quadrupole interaction that was of the same order of magnitude as the hyperfine interaction. Spin-Hamiltonian constants which describe the ESR spectrum were determined with the use of a computer. Electron irradiation at 77°K was not successful in producing Eu^{2+} in isomorphous CeO_2. In addition, crystals of ThO_2 and CeO_2 doped with trivalent thulium were also electron-irradiated at 77°K, but no change in the Tm valence was detected.

INTRODUCTION

FOR several years, it has been known that trivalent rare-earth ions incorporated into the cubic fluorite crystals CaF_2, SrF_2, BaF_2, and $SrCl_2$ can be reduced to the divalent state.[1-4] This conversion can be accomplished by either ionizing radiation,[1] metal vapor baking,[5] or solid-state electrolysis.[6] In the fluorite crystals, the rare earth occupies the cation site, which has eightfold cubic coordination. Apparently only rare-earth ions located in sites with cubic crystal field symmetry are reduced by irradiation. Even though the techniques of metal vapor baking and solid-state electrolysis produce much larger concentrations of divalent ions, these ions are also located in cubic sites. Irradiation-produced divalent rare-earth ions revert to the trivalent state upon thermal bleaching or uv illumination, while the other techniques produce more stable divalent ions.

Recently, we have shown that Tm^{3+} in sixfold-coordinated cubic sites of CaO (rock-salt structure) could be made divalent by irradiation at 77°K and that the divalent Tm was not stable at room temperature.[7] Experiments were then begun to determine what valence changes can be induced in a cubic host with tetravalent, rather than divalent, cations.

Cubic crystals of ThO_2 and CeO_2 doped with Tm_2O_3, which exhibited no ESR signals before irradiation, were irradiated at 77°K with 2-MeV electrons. The ESR

spectra of these crystals were observed at 77 and 4.2°K without allowing the crystals to warm. No Tm^{2+} or Tm^{4+} signals were detected in either host, although the resonance spectra of ions in either valence state should be easily observable. The presence of Tm in the ThO_2 crystal was indicated by the characteristic Tm blue thermoluminescence[8] emitted as the irradiated ThO_2 crystal was warmed to room temperature. It was concluded that irradiation at temperatures of 77°K or above does not produce valence changes in Tm-doped ThO_2 and CeO_2. The other rare-earth ion most likely to be reduced in these hosts is Eu, since Eu^{2+} represents a half-filled shell ($4f^7$) which is relatively stable. Although europium frequently occurs in the divalent state, it is initially trivalent in ThO_2 and CeO_2. Attempts were then made to form Eu^{2+} by irradiation and were successful in ThO_2, but not in CeO_2.

Eu^{2+} is isoelectronic to Gd^{3+}, and its ground state ($^8S_{7/2}$) is an orbital singlet. An electric field of any symmetry will not lift the spin degeneracy of this state to first order. However, due to admixtures of higher-lying states, small crystal field splittings are observed. When the crystal field has cubic symmetry, the eightfold spin degeneracy is split into two doublets (Γ_6 and Γ_7) and a quartet (Γ_8). If an axial distortion of the crystal field is present, the free-ion ground state is split into four doublets described by $|\pm M_J\rangle$. No matter what the symmetry, the splitting of the $4f^7$, $^8S_{7/2}$ ground state in previously observed hosts is usually small enough to enable all seven $\Delta M_J = \pm 1$ transitions to be observed in an X-band ESR experiment. In addition, the spin-lattice relaxation time of $4f^7$ ions is generally long enough that the ESR can be detected at room temperature. The ESR spectra of Gd^{3+} have been reported in ThO_2 and CeO_2 in both cubic and axially symmetric sites, although only the cubic splitting has been measured.[9-11] Similar spectra for the isoelectronic divalent europium in these crystals would not be unexpected.

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† Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.
‡ Oak Ridge Graduate Fellow from Vanderbilt University under appointment from the Oak Ridge Associated Universities.
§ Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.
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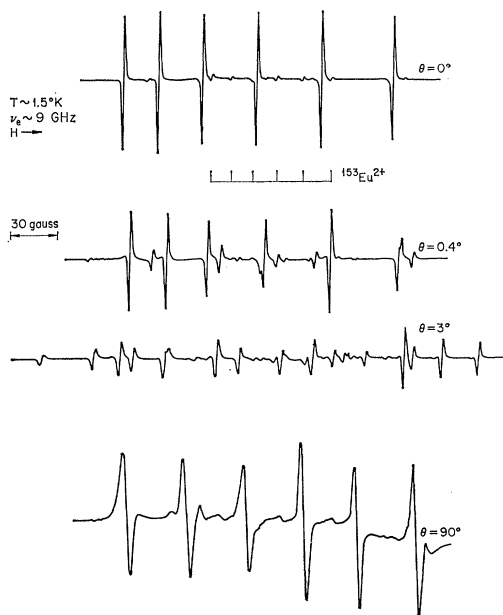[11] M. M. Abraham, L. A. Boatner, C. B. Finch, E. J. Lee, and R. A. Weeks, J. Phys. Chem. Solids **28**, 81 (1967).

T~1.5°K
$\nu_e\sim 9$ GHz
H →

30 gauss

$\theta=0°$

$\theta=0.4°$

$\theta=3°$

$\theta=90°$

$^{153}Eu^{2+}$

FIG. 1. ESR spectrum of $^{151}Eu^{2+}$ in ThO_2. Spectrum for one of the four trigonal $\langle 111 \rangle$ sites with H at various angles to the [111] axis.

EXPERIMENT

Crystals of ThO_2 and CeO_2 doped with Eu (up to 1-wt.% Eu_2O_3 in the growth solution) were grown from the high-temperature solvent $Li_2O \cdot 2WO_3$ by a method previously described.[12,13] No ESR signals were observed in the unirradiated crystals at temperatures down to 4.2°K, indicating the Eu was in the trivalent state (Eu^{3+} has a $^7F_0$ ground state and hence is diamagnetic). The crystals were irradiated at 77°K with 2-MeV electrons, and the resonance spectrum was examined at 77°K without an intervening warmup. No signals were observed in either host, but upon lowering the temperature to 4.2°K, Eu^{2+} signals were observed in ThO_2, but not in CeO_2. Although originally colorless, crystals of both hosts were blue-black after irradiation, and both exhibited pink thermoluminescence typical of Eu^{3+} when allowed to warm to room temperature. (The thermoluminescence intensity was weaker in the CeO_2, however.) After warm-up, the ThO_2 was slightly pink, while the CeO_2 was colorless. The Eu^{2+} in ThO_2 bleached slowly at room temperature and rapidly with uv illumination. Irradiated ThO_2 crystals that were stored in the dark for two weeks at room temperature still possessed a Eu^{2+} spectrum. Weak Eu^{2+} signals in ThO_2 could also be detected at 4.2°K after room-temperature β or ^{60}Co γ irradiation.

In contrast to previously observed cases of irradiation-produced divalency, the Eu^{2+} spectrum showed trigonal,

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rather than cubic, symmetry about the four $\langle 111 \rangle$ axes of the crystal. For each site, only one highly anisotropic $\Delta M_J = \pm 1$ transition was observed, indicating that the crystal field was so strong that at high temperatures the spin-lattice relaxation time was too short for a resonance spectrum to be observed, while at low temperatures only the $|M_J = \pm\frac{1}{2}\rangle$ doublet was populated. For an effective spin $\frac{1}{2}$, the observed g values ($g_{\parallel}\simeq 2$, $g_{\perp}\simeq 8$) showed that the resonance was between the levels of a ground doublet of an $S=\frac{7}{2}$ state ($4f^7$ electronic configuration), and the characteristic hyperfine structure definitely labeled the ion as europium.

A large nuclear quadrupole interaction made the angular variation of the hyperfine structure so complex that it was necessary to grow crystals with only one or the other of the two stable isotopes: ^{151}Eu ($I=\frac{5}{2}$, natural abundance 47.8%) or ^{153}Eu ($I=\frac{5}{2}$, natural abundance 52.2%). The enriched ^{151}Eu was 96.7% ^{151}Eu and 3.3% ^{153}Eu, while the enriched ^{153}Eu was 98.7% ^{153}Eu and 1.3% ^{151}Eu. The large anisotropy made it easy to separate the hyperfine spectra of the four different $\langle 111 \rangle$ sites. As expected for allowed ($\Delta M_J = \pm 1$, $\Delta M_I = 0$) transitions, the ^{151}Eu hyperfine spectrum showed six large lines at $\theta = 0°$, where θ denotes the angle the magnetic field makes with the [111] axis (Fig. 1). As θ was increased from $0°$, forbidden lines ($\Delta M_I \neq 0$) grew rapidly in intensity due to admixtures of the nuclear levels by the quadrupole interaction, while the allowed lines decreased, so that some of the forbidden lines became equal to, or larger than, the allowed lines at $\theta \simeq 1°$. For $\theta \simeq 3°$, almost all of the 36 possible $\Delta M_J = \pm 1$ transitions were observed. This complex pattern simplified as θ was increased further, so that by $\theta \simeq 15°$, a six-line hyperfine spectrum was again observed for this isotope and was maintained as θ was increased to 90°. Some of the small lines present in Fig. 1 are due to the 3.3%-abundant ^{153}Eu isotope.

The ^{153}Eu-enriched crystal also had a six-line hyperfine spectrum at $\theta = 0°$ (Fig. 2). In the region $0° < \theta < 10°$, the angular variation of the allowed lines (i.e., the six large lines at $\theta = 0°$) was unusual. Designating these lines at $\theta = 0°$ by the numbers 1–6, counting from low field, the innermost lines (3 and 4) moved toward the outside of the spectrum as θ was increased and approached lines 2 and 5, respectively. At $\theta = 4°$, line 3 was at a lower field than line 2, while line 4 coincided with line 5. With further increases in θ, lines 3 and 4 continued moving outward to superimpose with lines 1 and 6, respectively. At 10°, the three lines of each half of the spectrum coalesced. These two lines then split into three lines and large forbidden lines appeared, some of which superimposed as θ was further increased. At the same time, the allowed lines grew smaller, so that by $\theta \simeq 30°$, a 10-line hyperfine spectrum was observed for each site. This pattern was essentially maintained as θ was still further increased to $\theta = 90°$. The different hyperfine pattern for this isotope is not unexpected, since the ^{153}Eu quad-

rupole moment is 2.5 times larger than that of ^{151}Eu, and the magnetic moment is 2.26 times smaller. For both isotopes the linewidth varied with magnetic field orientation and was approximately 1 G at $\theta = 0°$ and 4 G at $\theta = 90°$.

The observed spectra were fitted to a spin Hamiltonian:

$$\mathcal{3C} = g_{||}\beta H_z S_z + g_{\perp}\beta[H_x S_x + H_y S_y] + A I_z S_z$$
$$+ B[I_x S_x + I_y S_y] + P[I_z^2 - \tfrac{1}{3}I(I+1)]$$
$$- (g_N)_{||}\beta_N H_z I_z - (g_N)_{\perp}\beta_N[H_x I_x + H_y I_y],$$

with $S = \tfrac{1}{2}$, $I = \tfrac{5}{2}$, and where an axially symmetric nuclear Zeeman term was included to account for any "pseudonuclear" interaction. Since the quadrupole interaction was found to be an appreciable fraction of the hyperfine interaction, the usual perturbation formulas for the transitions[14] could not be used and two computer programs were used to determine the spin-Hamiltonian parameters. The first program started with trial values for the spin-Hamiltonian parameters and computed the eigenvalues, eigenvectors, transition energies, transition probabilities, and derivatives of the transition energies with respect to each of the parameters and the angle θ, for any given magnitude and direction of the dc magnetic field. This program also labeled the transitions for use in a second program, which adjusted the parameters to bring the computed transitions as close as possible to the microwave energy.

A crystal containing one of the isotopes was mounted in the cavity so that the magnetic field could be rotated in the (110) plane. The symmetry of the $\langle 111 \rangle$ axial system in this plane allowed accurate determination of those values of θ, such that $\cos\theta = 1$, $\sqrt{\tfrac{2}{3}}$, $\sqrt{\tfrac{1}{3}}$, $\tfrac{1}{3}$, and 0. The measured line positions at these angles were sufficient to determine $g_{||}$, $g_{\perp}$, A, B, and $|P|$ for both isotopes as well as $|(g_N)_{\perp}|$ for ^{153}Eu and $|(g_N)_{||}|$ for ^{151}Eu.

In an attempt to determine $^{153}(g_N)_{||}$ and the sign of P relative to A and B, the line positions were measured at $0° < \theta \leq 2°$, where the lines were insensitive to $(g_N)_{\perp}$, but some were sensitive to $(g_N)_{||}$. Owing partly to the large anisotropy at these angles, the computer could use the evaluated parameters to determine the angle θ more accurately than it could be measured. Thus for a set of measurements at a given angle θ, two allowed lines whose derivatives with respect to P and $(g_N)_{||}$ were small were used to find a slightly different value of θ which would give better agreement between the computed and experimental line positions. With the improved angle θ, all line positions taken at that angle were used to determine $(g_N)_{||}$ and the relative sign of P. The positions of the forbidden lines in this region were most sensitive to changes in P and $(g_N)_{||}$. Unfortunately, not enough of the forbidden lines could be measured to determine the relative sign of P and a
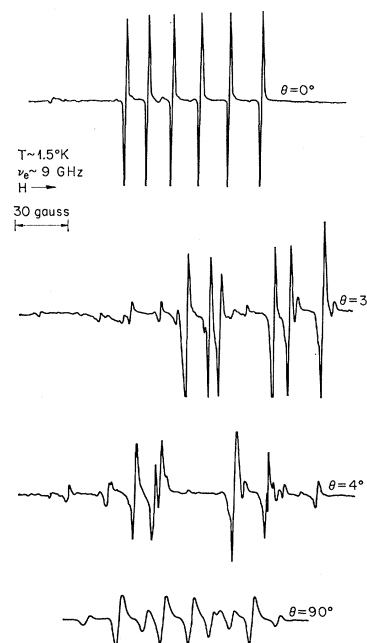
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FIG. 2. ESR spectrum of ^{153}Eu^{2+} in ThO$_2$. Spectrum for one of the four trigonal $\langle 111 \rangle$ sites with **H** at various angles to the [111] axis.

precise value of $(g_N)_{||}$ for ^{153}Eu. The absence of ^{151}Eu forbidden lines at large values of θ prevented determination of $(g_N)_{\perp}$ for this isotope.

The spin-Hamiltonian parameters given by the computer are presented in Table I. With these constants, the computed position of every line was within 1 G of the measured position.

For either isotope the values of $(g_N)_{||}$ and $(g_N)_{\perp}$ that gave the best fit to the data depended strongly on the sign of P. If P was chosen to have a different sign from A for ^{151}Eu, the computed value of $(g_N)_{||}$ was 1.5 ± 0.3, which agrees with the nuclear g value of 1.3852 measured by atomic beams.[15] If P was chosen to have the same sign as A, $(g_N)_{||} = -5.0 \pm 0.3$. Both sets of constants fit the data equally well, but it appears from the above that P probably has a different sign from A. If

TABLE I. Spin-Hamiltonian parameters for divalent europium in ThO$_2$. The choice of negative signs for A and B conforms with that of Baker and Williams (see Ref. 20). The sign of P was chosen to give the more likely value of $^{151}(g_N)_{||}$.

	^{151}Eu		^{153}Eu	
$g_{||}$	1.9678 ± 0.0005		1.9678 ± 0.0005	
$g_{\perp}$	7.867	± 0.002	7.867	± 0.002
A (MHz)	-96.3	± 0.2	-42.6	± 0.1
B (MHz)	-407.9	± 0.8	-180.0	± 0.8
P (MHz)	$+23.3$	± 0.3	$+59.6$	± 0.5
$(g_N)_{||}$	1.5	± 0.3	1.0	± 2.3
$(g_N)_{\perp}$	$\cdots$		-7.6	± 0.8

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P has the same sign as A, a large pseudonuclear interaction would have to be present to explain the discrepancy in $(g_N)_{\parallel}$. Since the quadrupole moments of both ions have the same sign, the sign of P for both isotopes is the same. If ^{153}P is assumed to have a different sign from A, the calculated $^{153}(g_N)_{\perp}$ is -7.6 ± 0.8. For ^{153}P having the same sign as A, $^{153}(g_N)_{\perp} = +6.7 \pm 0.9$. Neither $(g_N)_{\perp}$ value is close to the expected g_N value of 0.6117,[15] but both values fit the data equally well. The ambiguity in the signs of the parameters could possibly be removed by further data (locating more forbidden lines) on more heavily doped samples. However, an ENDOR study of these crystals would be more profitable since it would give not only the signs, but more accurate values for all the constants, except the electronic Zeeman terms.

DISCUSSION

The present work is the first case in which the groundstate splitting of a $4f^7$ ion is so large that it can be described with an effective spin of $\frac{1}{2}$. The exceptional strength of the crystal field is also indicated by the unusually short spin-lattice relaxation time for an S-state ion. All previously observed spectra of Eu^{2+} or Gd^{3+} could be observed at room temperature. A large crystal field splitting has also been observed for Fe^{3+} $(3d^5,{}^6S_{5/2})$ and is routinely found for Cm^{3+} and Am^{2+} $(5f^7,{}^8S_{7/2})$.[16] It is also the first case in which electron or γ irradiation has produced a divalent rare-earth ion in an axial crystal field as well as in a tetravalent site. In the only other case where a divalent rare earth was produced in a noncubic site $(Tm^{2+}$ in $BaF_2)$ [17] the authors employed both γ and optical irradiation. A model which explains the $\langle 111 \rangle$ axial symmetry and provides the required charge compensation is a substitutional Eu^{2+} ion with a nearest-neighbor O^{-2} vacancy. However, the validity of the model cannot be proved by the available data.

For a $J = \frac{7}{2}$ ion whose ground state in an axial crystal field is described by an effective spin of $\frac{1}{2}$:

$$g_{\parallel} = 2\lambda \langle M_J = \tfrac{1}{2} | J_z | M_J = \tfrac{1}{2} \rangle = \lambda,$$
$$g_{\perp} = \lambda \langle M_J = \tfrac{1}{2} | J_+ | M_J = -\tfrac{1}{2} \rangle = 4\lambda,$$

where λ is the Landé g factor. Ignoring relativistic and diamagnetic effects, $\lambda = 2$ for Eu^{2+}, and therefore $g_{\parallel} = 2$ and $g_{\perp} = 8$. The agreement of these values with the observed g values for ThO_2:Eu is proof that the Eu is divalent with a $| M_J = \pm \frac{1}{2} \rangle$ doublet lowest, and that the dominant second-order crystal field parameter $B_2{}^0$ is positive. The departure of the measured $g_{\parallel}$ from 2.0005 (the value of 2 for the $^8S_{7/2}$ state corrected for relativistic and diamagnetic effects)[18] is larger in this host

than for other Eu-doped crystals. Such deviations are usually explained as due to admixtures of excited states. Judd and Lindgren[18] find that spin-orbit coupling with the $^6P_{7/2}$ state reduces the λ to 1.9933 and clearly another mechanism is needed. Another indication of admixtures of higher-lying J manifolds is the departure of $g_{\perp}A/g_{\parallel}B$ from unity.[19] The measured values give $g_{\perp}A/g_{\parallel}B = 0.944$ for ^{151}Eu and 0.946 for ^{153}Eu.

The ratios of the hyperfine interaction parameters

$$^{151}A/^{153}A = 2.261 \pm 0.010, \quad ^{151}B/^{153}B = 2.266 \pm 0.014$$

are in good agreement with the ratios of the magnetic moments

$$^{151}\mu/^{153}\mu = 2.2632 \pm 0.0026, \quad ^{151}\mu/^{153}\mu = 2.26505 \pm 0.00042$$

found by ENDOR[20] and atomic beams,[15] respectively. The ratio of the quadrupole interaction parameters

$$^{153}P/^{151}P = 2.56 \pm 0.05$$

may be compared with the ratio of the quadrupole moments

$$^{153}Q/^{151}Q = 2.54$$

found by atomic beams[21] and optical spectroscopy.[22] Much weaker quadrupole interactions for Eu^{2+} in $PbCl_2$ were found by Vrehen and Volger[23] and for Eu^{2+} in CaF_2 by Baker and Williams.[20] The latter give

$$^{153}Q/^{151}Q = 2.58 \pm 0.02.$$

These values agree within experimental error.

It was necessary to consider the nuclear Zeeman term in the spin-Hamiltonian to be axially symmetric. Another microwave frequency was not available to check the linear magnetic field dependence of this term; however, the only other interactions known which could possibly affect the spectrum are the octopole and the high-order $A'I^mS^n$ interactions.[20] For an effective spin $S = \frac{1}{2}$ state, only the octopole, $A'I^3S$, and $A''I^5S$ terms would contribute to the Hamiltonian. All these additional terms (octopole and I^mS^n) have been found[20] to be quite small for Eu^{2+}, and were therefore neglected. The pseudonuclear interaction arises from admixtures of other levels within the J manifold by a combination of the magnetic field, hyperfine, and quadrupole interactions.[4,24] The largest of these interactions, involving

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the magnetic field, will cause much larger admixtures when the direction of the field is not parallel to the symmetry axis of the site. The fact that the $(g_N)_{||}$ values for both isotopes are close to the expected values, while $(g_N)_\perp$ for ^{153}Eu is greatly different, confirms this expectation. If good values for the nuclear g values can be obtained, it should be possible to calculate a rough value

of the separation of the $|\pm\frac{1}{2}\rangle$ doublet from the next nearest $|\pm\frac{3}{2}\rangle$ doublet.

Fine Structure Observed in Modified X-Ray Scattering by Boron

N. G. ALEXANDROPOULOS AND G. G. COHEN

Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

Using a double-crystal spectrometer, two portions of the spectrum of Cu $K\alpha_1$, $K\alpha_2$ radiation scattered by boron have been recorded. One portion is near the Rayleigh peaks; the other portion is at a distance of about 180 eV from the Rayleigh peaks. Several discontinuities have been noted in the first region. A definite double line has been observed in the second region at a distance from the Rayleigh lines which corresponds closely to the energy required for a $1s$-$2p$ electron transition. The widths of the observed lines are in agreement with the K boron emission lines. No conclusive results have yet been obtained with regard to the selection rules. It is not clear that the process under investigation is a three-level transition process.

INTRODUCTION: CURRENT STATUS OF PROBLEM

SINCE the discovery of the Compton effect, physicists have expected this phenomenon to be useful in the study of the solid state. Early experimental data encouraged their hopes. However, little success is evident as yet in the application of modified x-ray scattering to the study of solids. Recent advances in instrumentation have improved the possibility of progress in this direction.

The fine structure of the Compton spectrum was first reported in a series of articles by Davis[1,2] and his co-workers, and by Mitchell[3] in 1929. Their results were challenged by Bearden[4] a year later. DuMond[5] discussed theoretically the existence of an x-ray Raman effect in terms of a series of sharp lines related to electron transitions to unfilled energy levels in the atom. He considered the contradictions in the literature to be due to the very low intensity of the effect. In 1936, Sommerfeld[6] studied inelastic scattering of x rays by bound electrons and predicted the existence of discrete Raman lines. He did not discuss the associated selection rules, but he did confirm theoretical studies by Schnaidt[7] on the relative intensities of the Rayleigh and Raman lines. According to Schnaidt, the first Raman line

(corresponding to the $n=1$ to $n=2$ transition) in the most favorable case (when the Compton shift is equal to the binding energy) has an intensity of $\frac{1}{5}$ of the Rayleigh line. Successive Raman lines diminish rapidly in intensity in proportion to $1/n^3$.

In recent years, the story has been one of repeated observation of Smekel-Raman-type lines and challenges to these observations. Das Gupta,[8] in 1959, using a bent Mica Cauchois spectrograph and a photographic exposure method, reported the existence of Raman-type modified lines for graphite, aluminum, and beryllium. Weiss,[9] in 1965, repeated the Das Gupta measurements on graphite, beryllium, and lithium fluoride with a Norelco fluorescence spectrometer and did not confirm Das Gupta's findings. It should be noted that the spectrometer used by Weiss did not appear to provide the resolution necessary to observe a fine structure in Compton spectra. Work by Faessler and Mühle,[10] in 1966, carried out with an experimental arrangement similar to that of Das Gupta, confirmed Das Gupta's results. Suzuki[11] studied the x-ray Raman effect in 1967 with a single flat-crystal spectrometer and Cu $K\alpha$ radiation from a high-intensity rotating anode tube. His results, with respect to the position of the Raman lines, are in agreement with theoretical predictions of Mizuno and Ohmura.[12] Mizuno and Ohmura predicted that the Raman spectrum should have

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