

## Hyperfine Structure in Europium Metal\*

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Mössbauer resonance experiments were performed on europium metal, using the 21.7-keV gamma ray in  $\text{Eu}^{151}$ . The Néel point of 87°K was confirmed. Above this temperature a single line was observed and attributed to paramagnetic relaxation. At 4.2°K a six-line spectrum was found. Analysis yielded a spin of  $\frac{7}{2}$  and a moment of  $+2.53 \pm 0.03$  nm for the 21.7 keV excited state, an internal field of  $264 \pm 8$  kG, and an isomeric chemical shift of  $-0.81 \pm 0.03$  cm/sec, relative to  $\text{Eu}_2\text{O}_3$ . This is consistent with an electronic level  $4f^7 6s^2$ ,  $^8S_{7/2}$  for the europium atom. The effect of nuclear deformation on isomeric chemical shifts is considered, and it is concluded that  $\text{Eu}^{151}$ , with a moderately deformed ground state, has a less deformed excited state at 21.7 keV.

### I. INTRODUCTION

EXPERIMENTAL determination of hyperfine magnetic fields in metals has become an important factor in elucidating the mechanisms of ferromagnetism. The requirement that they reproduce the magnitude and sign of the observed magnetic field at the nucleus is a sensitive and stringent test of electronic wave functions associated with magnetic behavior. None of the available experimental methods (nuclear magnetic resonance, Mössbauer absorption, heat capacity measurements, nuclear orientation, and angular correlations) are really generally applicable, and they share the common fault of failing completely in certain situations. Still, enough workable cases have been found to provide data on about twenty hyperfine fields, and indeed these cases are sufficiently representative that one may begin now to speak of "trends."

Europium exhibits magnetic behavior, becoming antiferromagnetic at 87°K and possibly ferromagnetic at lower temperatures. It is one of the more interesting of the rare earths because the atomic level is presumably  $4f^7 6s^2$ ;  $^8S_{7/2}$ , and the hyperfine field, as in other half-filled shells, has more complex origins than simply the orbital angular momentum of the unperturbed lowest level. Moreover, neutron diffraction data indicate that europium has a spiral antiferromagnetic structure.<sup>1</sup>

We have observed hyperfine structure in europium by means of Mössbauer absorption experiments on  $\text{Eu}^{151}$ . Several spectra were taken near the Néel point to delineate the main features of the temperature dependence there, but no systematic study was made of the temperature range below 87°K, where collective magnetic behavior is observed. We have, rather, concentrated on characterizing the spectrum at 4.2°K, to derive the hyperfine field and nuclear moments.

### II. EXPERIMENTAL

The apparatus is described in detail elsewhere. It consists of a three-walled double-Dewar system into which a "drive capsule" holding the source and absorber is inserted. The Doppler velocity is produced and detected by electromechanical transducers, also in the capsule. The source can be placed within a few cm of the detector, and gamma rays pass through thin Mylar and beryllium windows. The inner Dewar retains liquid helium for about 40 h.

A source of  $\text{Gd}^{151}$  in a lattice of  $\text{Eu}_2\text{O}_3$  (enriched in  $\text{Eu}^{153}$ ) provided a single line for this work. The  $\text{Eu}^{+3}$  ion has a  $^7F_0$  level lowest; consequently there is no hyperfine structure in first approximation.<sup>2,3</sup> The 21.7-keV  $\gamma$  ray has a mean life of  $\sim 10^{-8}$  sec and a recoil-free fraction in this source of at least 0.36 at room temperature.<sup>4</sup>

Europium is chemically the least stable of the rare earth metals. It is violently oxidized by water and decomposes to a yellow oxide in a few minutes if left unprotected in the air. The absorbers used in this work were rolled (to 0.002 in.) and cut under kerosene, rinsed in ether, and immediately sealed in a sandwich of 0.001-in. Mylar tape. When not in use, they were stored at 77°K.

### III. RESULTS

Europium is one of the "softest" rare earth metals in many ways, with anomalously low transition points,<sup>5</sup> and one might estimate its Debye temperature to be no more than 140° at most. Although it was not possible to derive Debye-Waller factors from this work, the magnitude of the absorption was consistent with a Debye temperature in this range. The highest temperature at which a spectrum was taken was 100°K. As this is well above the Néel point, the hyperfine field might be expected to be averaged to zero by paramagnetic

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<sup>1</sup> C. E. Olsen, N. G. Nereson, and G. P. Arnold, *Suppl. J. Appl. Phys.* **33**, 1135 (1962).

<sup>2</sup> R. J. Elliott, *Proc. Phys. Soc. (London)* **B70**, 119 (1957).

<sup>3</sup> B. R. Judd, C. A. Lovejoy, and D. A. Shirley, *Phys. Rev.* **128**, 1733 (1962).

<sup>4</sup> D. A. Shirley, M. Kaplan, R. W. Grant, and D. A. Keller, *Phys. Rev.* **127**, 2097 (1962).

<sup>5</sup> Karl A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand, Inc., Princeton, 1961), p. 23.

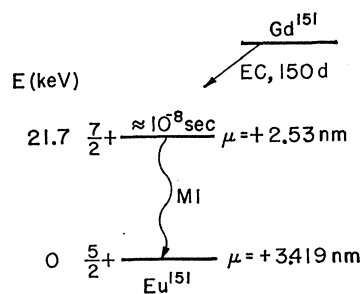


FIG. 1. The isomeric levels of  $\text{Eu}^{151}$  discussed in this paper.

relaxation, producing a single-line spectrum. Indeed only one line was observed, at a relative velocity<sup>6</sup> of  $-0.82 \pm 0.05$  cm/sec. Thus, the nuclear level spacing between the isomeric and the ground states of  $\text{Eu}^{151}$  is larger in  $\text{Eu}_2\text{O}_3$  than in Eu metal. All the lower temperature points were also shifted by  $\sim -0.8$  cm/sec, indicating that the magnetic transitions induced no gross change in the 6s (conduction) electron density.

Figure 1 shows the isomeric levels of  $\text{Eu}^{151}$ . Data from several temperatures near the Néel point are shown in Fig. 2. As the temperature was lowered to  $77^\circ\text{K}$  the line broadened to a complex but unresolved hfs pattern. At  $100^\circ$  the linewidth was 0.35 cm/sec, near the natural width (although the lifetime of the 21.7-keV state has not been determined directly, a lower limit of 9.2 nsec has been set.<sup>4</sup> If we assume that any excess linewidth in the data of reference 4 arises from unresolved hyperfine structure, we may set an upper limit of  $\sim 15$  nsec on the transition lifetime. Then the minimum possible experimental linewidth is in the range 0.14–0.23 cm/sec). Thus, the broadening with decreasing temperature may be associated with the onset of antiferromagnetism. The great difference between the absorption spectra at  $86^\circ$  and  $90^\circ$  (Fig. 2) provides confirmation of the Néel point of  $87^\circ\text{K}$  and indicates that europium is paramagnetic at higher temperatures.

The magnetic behavior of europium below  $87^\circ\text{K}$  is apparently complicated and not well understood. Before Mössbauer experiments can be usefully applied to this problem, it is necessary to characterize the nuclear Zeeman spectrum. Thus, an experiment was done at  $4.2^\circ\text{K}$ , where it was hoped that the hyperfine field would be large enough to resolve the pattern. The spectrum shown in Fig. 3 was obtained. It consists of 4 equally spaced strong lines of equal intensity, centered around  $-0.81 \pm 0.03$  cm/sec, and two lines of about  $\frac{1}{4}$  this intensity with slightly greater spacing.

#### IV. NUCLEAR MOMENTS AND THE HYPERFINE FIELD

A hyperfine field can be derived from the spectrum at  $4.2^\circ\text{K}$  provided that the nuclear  $g$  factor for each state is known. First, we observe (Fig. 3) that there is no evidence for quadrupole splitting (i.e., the spectrum is

<sup>6</sup> We are using the peculiar, but universal, sign convention that two objects moving toward one another have positive relative velocity.

completely symmetrical about  $-0.81$  cm/sec). Thus, the positions of the hfs levels in either isomeric state are given by a Hamiltonian of the form  $AM_I$ . For a given set of nuclear spins and a given sign for the magnetic-moment ratio in the two isomeric states, the totality of all possible hyperfine spectra is given by a "g-factor diagram," an example of which is shown in Fig. 4. The ordinate is the ratio of  $g$  factors: its range is zero to infinity. The abscissa has dimensions of energy. The experimental spectrum of  $\text{Eu}^{151}$  falls on the horizontal line  $A-A'$ . The relative positions of the Zeeman components on this line are exactly equal to their relative positions in the spectrum. The intensities also fit very well, as shown by the theoretical curve in Fig. 3. The two very weak outside lines indicated on the diagram were not searched for. We note that the experimental  $g$ -factor ratio falls at a remarkably fortunate value, allowing the four rather sharp central lines to absorb 88% of the transition intensity.

The ground-state spin and magnetic moment were known<sup>7</sup> to be  $\frac{5}{2}$  and  $+3.419$  nm. The 21.7 keV transition is magnetic dipole.<sup>8,9</sup> Thus, the excited-state spin had to be  $\frac{3}{2}$ ,  $\frac{5}{2}$ , or  $\frac{7}{2}$ . There was very good evidence from nuclear spectroscopy that the  $\frac{7}{2}$  choice was correct.<sup>10</sup> Indeed of the six possible combinations of excited-state spin and sign of the excited-state magnetic moment, only the  $\frac{7}{2}$ , + combination (Fig. 4) fits the data, and this fits only position  $A-A'$ , for which  $g_1/g_0 = +0.528 \pm 0.005$ . Thus, the excited-state spin is  $\frac{7}{2}$ , and the magnetic moment is  $+2.53 \pm 0.03$  nm. The corresponding hyperfine field is  $264 \pm 8$  kG.

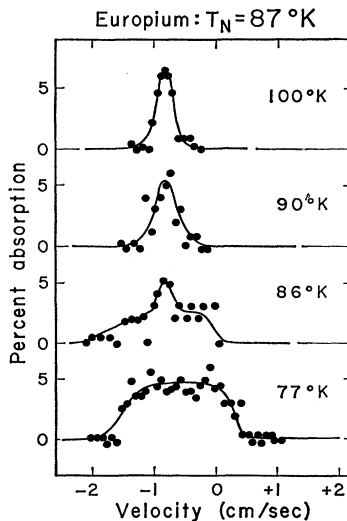


FIG. 2. The resonant absorption spectra of  $\text{Eu}^{151}$  in europium metal at several temperatures near the Néel point of  $87^\circ\text{K}$ .

<sup>7</sup> F. M. Pichanick, P. G. H. Sandars, and G. K. Woodgate, Proc. Roy. Soc. (London) **A257**, 277 (1960).

<sup>8</sup> V. S. Shirley and J. O. Rasmussen, Phys. Rev. **109**, 2092 (1958).

<sup>9</sup> W. T. Achor, W. E. Phillips, J. I. Hopkins, and S. K. Haynes, Phys. Rev. **114**, 137 (1959).

<sup>10</sup> N. M. Anton'eva, A. A. Bashilov, B. S. Dzelopov, and B. K. Preobrazhenskii, Izv. Akad. Nauk SSSR Ser. Fiz. **22**, 135 (1958) [translation: Bull. Acad. Sci. USSR **22**, 134 (1958)].

It is customary to separate atoms in metals conceptually into ion cores and conduction electrons. In europium the electronic configuration is  $4f^7 6s^2$ , which is thought to produce a  $4f^7, {}^8S_{7/2}$  ion core, with the two  $6s$  electrons going into the conduction band. If the situation is really this simple and there are no effects such as conduction-electron polarization, the hyperfine field should be just that produced by the  ${}^8S_{7/2}$  level. A calculation of this field from fundamentals is not straightforward, but a reasonable estimate may be obtained from electron paramagnetic resonance data on  $\text{Eu}^{+2}$ , which has the  ${}^8S_{7/2}$  level lowest. Values of  $A_{151}$  in the  $\text{Eu}^{+2}$  spin-Hamiltonian range from 0.00308 to 0.00341  $\text{cm}^{-1}$  for different environments,<sup>11,12</sup> indicating hyperfine fields between 311 and 343 kG. The agreement with this experiment is rather good, considering, (1) the sensitivity of the field at the nucleus to configuration mixing and conduction-electron polarization; (2) the approximate nature of the comparison; and (3) that the experiment was done at 4.2°K (this was the bath temperature; the sample may have been a few tenths of a degree warmer) rather than absolute zero, and the field must be less than the saturation field. We thus interpret the hyperfine field as arising from the  ${}^8S_{7/2}$  electronic level. Of course it is also possible that large core-polarization or conduction-electron polarization effects are present which change the sign of the net hyperfine field. This can be settled by determination of the sign. At present we can say that the magnitude of the field does not require such effects.

#### V. ISOMERIC CHEMICAL SHIFT AND NUCLEAR DEFORMATION

The chemical shift in  $\text{Eu}^{151}$  between the metal and the sesquioxide (i.e., between  $\text{Eu}^0$  and  $\text{Eu}^{+3}$ ) is the second largest yet measured, the largest being in  $\text{Au}^{197}$ . In

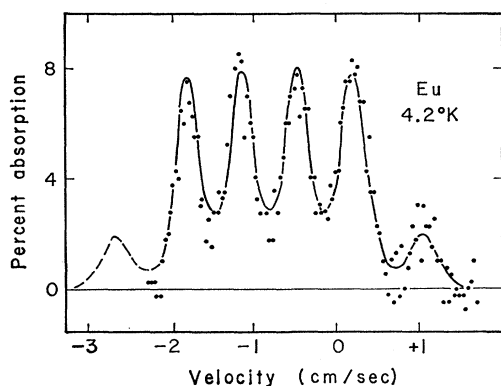


FIG. 3. The resonant absorption spectrum of  $\text{Eu}^{151}$  in europium metal at 4.2°K. The sweep did not go to high enough velocities to detect the weak line at  $-2.6$   $\text{cm/sec}$  in this run. In other runs this line was observed. The theoretical curve is for a  $g$ -factor ratio of 0.528.

<sup>11</sup> B. Bleaney and W. Low, Proc. Phys. Soc. (London) **A68**, 55 (1955).

<sup>12</sup> W. Low, Phys. Rev. **106**, 1827 (1956).

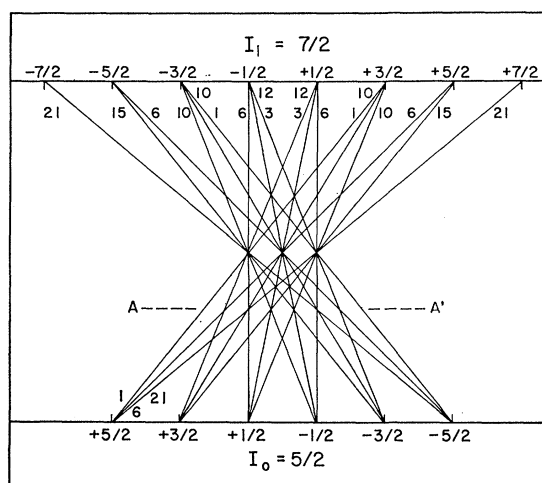


FIG. 4. The  $g$ -factor diagram for a dipole transition between two states of spins  $\frac{7}{2}$  and  $\frac{5}{2}$ , having magnetic moments of the same sign. The line  $A-A'$  fits the  $\text{Eu}^{151}$  spectrum. Numbers near lines denote relative intensities.

these two nuclei the large shift arises from a combination of  $6s$  electron transfer plus unusual nuclear effects. In  $\text{Au}^{197}$  the nuclear effect is core excitation in the excited state<sup>13,14</sup>; in  $\text{Eu}^{151}$ , on the edge of the collective nuclear region,<sup>3</sup> the most plausible interpretation is that the excited state is less deformed than is the ground state.

The isomeric chemical shift is given approximately by the expression<sup>15,16</sup>

$$\delta E = \frac{2\pi}{5} Z e^2 R^{2-2\rho} (\Delta \langle r^{2\rho} \rangle) [\Delta \psi(0)^2]. \quad (1)$$

Here  $R$  is the nuclear radius. The term in  $\Delta \psi(0)^2$  for the  $\text{Eu}-\text{Eu}_2\text{O}_3$  system is approximately twice the  $6s$  electron density at the nucleus, because  $\text{Eu}^0$  has two  $6s$  electrons which  $\text{Eu}^{+3}$  lacks. This electron density at the nucleus in the metal should be the same order of magnitude as that in the free atom, which is given by the expression<sup>17</sup>

$$\psi(0)^2 = (1/\pi a_0^3) (Z_i Z_a^2 / n_a^3) (1 - d\sigma/dn). \quad (2)$$

There are not enough data available to obtain  $\psi(0)^2$  for europium directly from experiment; instead we have

<sup>13</sup> A. Braunstein and A. de-Shalit, Phys. Letters **1**, 264 (1962).

<sup>14</sup> D. A. Shirley, Phys. Rev. **124**, 354 (1961). The new model for  $\text{Au}^{197}$  in reference 13 requires that the isomeric shifts in  $\text{Au}^{197}$  be interpreted using core-excitation wave functions. The extent of core deformation can be deduced by the methods outlined here and in the present paper.

<sup>15</sup> S. De Benedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters **6**, 60 (1961).

<sup>16</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

<sup>17</sup> H. Kopfermann, *Nuclear Moments*, translated by E. E. Schneider (Academic Press Inc., New York, 1958), p. 127 ff. This reference gives a thorough discussion of the Fermi-Segrè formula and more recent modifications as well as references to the original literature.

interpolated this quantity, which should vary smoothly with  $Z$ , between atoms with alkali-like configurations, for which it may be determined directly.<sup>17</sup> This procedure gives

$$\psi(0)^2 = 5 \times 10^{25} \text{ cm}^{-3}, \quad (3)$$

per 6s electron. From Eqs. (1) and (3), with the measured shift of 0.81 cm/sec, we obtain

$$\Delta \langle (r/R)^{2\rho} \rangle = 0.0012, \quad (4)$$

using  $R = 1.2A^{1/3} = 6.4\text{F}$ , with the ground state "larger" than the excited state. Because  $\text{Eu}^{151}$  is in a transition region there is no straightforward procedure available for explaining the observed value of  $\Delta \langle r^{2\rho} \rangle$ . Rather than presenting no explanation at all, we offer two possible, albeit crude, tentative interpretations. It should be clearly understood that these interpretations are speculative and are at best considerable oversimplifications of the problem. The procedure then is to approach the problem from the point of view of the two limiting cases, the nuclear shell model and the collective model.

The simple shell model can account for this size difference only by invoking "hole" states to give the observed sign. To make a shell-model calculation, we assume (1) that the two states correspond to single holes in the  $d_{5/2}$  and  $g_{7/2}$  shells (holes are necessary to give the right sign), and (2) that the nuclear potential is a finite square well. With a nuclear radius of 6.4 F, we find, using the radial moments calculated by Eisinger and Jaccarino,<sup>18</sup>  $\Delta \langle r^2 \rangle = 7.55\text{F}^2$  for the odd proton, or  $0.12\text{F}^2$  for the entire nucleus. The quantity  $\Delta \langle (r/R)^2 \rangle$  is, thus, 0.003. This is somewhat larger than the experimental value in Eq. (4) (the two quantities are roughly comparable because the relativistic parameter,  $\rho$ , has the value 0.89, close to 1, for europium). Thus, the single-particle shell-model approach gives the right order of magnitude but the wrong sign, if we do not invoke "hole states."

Another possible explanation for the observed value of  $\Delta \langle (r/R)^{2\rho} \rangle$  may be obtained using the collective coordinates of the entire nucleus. Europium-151 is situated on the edge of the collective nuclear region, having an intrinsic deformation of  $\delta = +0.12$  in its ground state. This was calculated from the intrinsic quadrupole moment<sup>3</sup> of  $+2.66 \text{ b}$ , using the relation<sup>19</sup>

$$Q_0 = \frac{2}{5} \delta Z R_0^2 (1 + \delta/2 + \dots). \quad (5)$$

To calculate the effect of nuclear deformation on the isomeric shift, we may approximate a prolate deformed nucleus by a uniformly charged ellipsoid bounded by the surface

$$R = R_0 [1 + \alpha P_2(\cos\theta)], \quad (6)$$

with  $\alpha > 0$ . The volume is equal to that of a sphere of radius  $R_s = R_0(1 - \alpha^2/4)$ , to terms in  $\alpha^2$ . For the ellipsoid the

average-square radius is given by  $\langle R^2 \rangle = R_0^2(1 + \alpha^2/2)$ , again to order  $\alpha^2$ . Thus, in going from a spherical to an ellipsoidal shape a nucleus experiences a change in its second radial charge moment of  $\alpha^2 R_s^2$ , where  $R_s$  is the radius of the spherical nucleus, as defined above. Comparison with Eq. (1) yields an isomeric shift of

$$\delta E = -\frac{2\pi}{5} Z e^2 \Delta \psi(0)^2 R_s^2 \Delta(\alpha^2), \quad (7)$$

in nonrelativistic approximation, accompanying a change in nuclear deformation between the isomeric states.

Equation (7) has a very simple physical interpretation, and should be adequate for most situations, including the case of  $\text{Eu}^{151}$ . In particular we note that, by combining Eqs. (5) and (7), together with the relation between the spectroscopic and intrinsic quadrupole moments<sup>20</sup> (and noting that our  $\alpha$  is  $\frac{2}{3}\delta$ ), one can derive explicit expressions relating the isomeric shift to either the quadrupole moments or to the deformations of the two states. In some cases (i.e., for very heavy nuclei) the nonrelativistic approximation may not be sufficiently accurate. It may then be profitable to use the results of Wilets, Hill, and Ford,<sup>21</sup> who have considered the effect of nuclear deformation on isotope shifts in optical spectra in much more general terms. Lardinois<sup>22</sup> has applied these results to optical isomeric shifts. In our notation the isomeric shift in a Mössbauer resonance spectrum becomes

$$\delta E = -\frac{2\pi}{5} Z e^2 \frac{3}{2\rho+1} R_s^2 \Delta \left[ \sum \psi(0)^2 \right] \times \Delta \left\{ \alpha^2 \left[ 1 + \frac{2}{21} (2\rho+3)\alpha + \dots \right] \right\}. \quad (8)$$

We write the electron density term as a sum to emphasize that for heavy nuclei (high  $Z$ ) one must consider all electrons which have a finite density at the nucleus, including the  $s$ -like small component of relativistic  $p_{1/2}$  electrons. As  $\rho$  approaches unity Eq. (8) reduces to Eq. (7) to order  $\alpha^2$ , as it should.

From the above discussion we find  $\Delta(\alpha^2) = 0.0011$  for  $\text{Eu}^{151}$ , with the ground state more deformed than the excited state. The intrinsic deformation of  $\delta_0 = +0.12$  corresponds to an  $\alpha_0$  of  $+0.08$ . Thus,  $\alpha_1 = +0.07$  on this model. It is interesting to attempt an explanation for the decrease of deformation in one of the isomeric levels. This nucleus must be very delicately balanced with respect to deformation, and it seems unlikely that

<sup>20</sup> A. Bohr and B. R. Mottelson, in *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (Interscience Publishers, Inc., New York, 1955).

<sup>21</sup> L. Wilets, D. L. Hill, and K. W. Ford, *Phys. Rev.* **91**, 1488 (1953).

<sup>22</sup> J. Lardinois, *Nucl. Phys.* **15**, 522 (1960).

<sup>18</sup> J. Eisinger and V. Jaccarino, *Rev. Mod. Phys.* **30**, 528 (1958).

<sup>19</sup> B. R. Mottelson and S. G. Nilsson, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Skr.* **1**, No. 8 (1959).

an unequivocal explanation can be given without first considering the theoretical situation very carefully. Perhaps the slightly larger increase with deformation of the energy of the  $\frac{7}{2}^+(404)$  Nilsson orbital<sup>19</sup> over that of the  $\frac{5}{2}^+(402)$  orbital can account for this result. Again a  $d_{5/2}$  orbital is much smaller than a  $g_{7/2}$  orbital, and it may be able to participate more in collective motions of the nucleus, including deformation. A similar situation is discussed by Mottelson and Nilsson<sup>19</sup> in the case of  $\text{Eu}^{153}$  and they suggest that the 98-keV excited state of that nucleus may have a smaller eccentricity than the ground state.

It is most probable that the true explanation lies between these two extremes. In fact it seems likely that the two effects (single-particle and collective) might compete, since the single-particle calculation alone gives the wrong sign, with the collective effects being slightly stronger. Thus, for example, the difference in deformation may even be greater (perhaps the excited state is undeformed), with much of this effect on  $\langle r^{2\rho} \rangle$  being

cancelled out by the effect of the single-particle  $g_{7/2}$  state.

Again we emphasize that this interpretation involves rather substantial approximations, including that of the  $6s$  electron density in europium metal. On the nuclear side it should be realized that, while the simple deformation picture is probably the best that can be used at present,  $\text{Eu}^{151}$  is in a transition region where no simple model is clearly applicable and a firm interpretation of the shift must be postponed until this transition region can be understood.

*Note added in proof.* The half-life of the 21.7-keV level in  $\text{Eu}^{151}$  has recently been measured as<sup>23</sup>  $9.5 \pm 0.5$  and  $9.3 \pm 0.7$  msec.<sup>24</sup> Our estimates in this paper of  $9.2 < \tau < 15$  would correspond to a half-life of  $8.4 \pm 2.1$  msec, in good agreement.

<sup>23</sup> D. J. Horen, H. H. Bolotin, and W. H. Kelly, *Bull. Am. Phys. Soc.* **8**, 127 (1963).

<sup>24</sup> A. C. Li, O. Kistner, and S. Monaro, *Bull. Am. Phys. Soc.* **8**, 332 (1963).

## Photoluminescence of Nitrogen-Exciton Complexes in $6H$ SiC

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The photoluminescence of N-doped  $6H$  SiC reveals two distinct edge emission spectra, a consequence of the existence of two kinds of nitrogen-exciton complexes. This paper describes the recombination radiation of excitons bound to nitrogen ions, complementing the previously reported recombination radiation of excitons bound to neutral nitrogen. By combining data from the two spectra, we are able to estimate ionization energies of 0.17, 0.20, and 0.23 eV, for the three inequivalent nitrogen donors. Several phonon energies can be determined, and these are compared with known phonon energies in  $6H$  SiC. A 90-meV phonon apparently represents a localized vibrational mode. Quenching of edge emission in impure samples is observed, and attributed to exciton hopping. Thermally excited states of the nitrogen-exciton complexes appear to be due to the valley-orbit splitting associated with a sixfold conduction-band degeneracy. A splitting of some of the states is attributed to the Jahn-Teller effect.

### I. INTRODUCTION

ULTRAVIOLET illumination of  $N$ -doped  $6H$  SiC creates excitons which may be captured by neutral or by singly ionized nitrogen, forming four-particle or three-particle nitrogen-exciton complexes. (The ion is considered to be one particle, and the complexes consist of the ion plus either three or two electronic particles.) The complexes decay by electron-hole annihilation, emitting photons, and, in most cases, one or more phonons. The four-particle luminescence spectrum, which lies within 0.14 eV of the exciton energy gap, has been reported by Choyke and Patrick<sup>1</sup> (abbreviated CP). The three-particle spectrum lies at somewhat lower energies, and is described in this paper.

<sup>1</sup> W. J. Choyke and Lyle Patrick, *Phys. Rev.* **127**, 1868 (1962).

Exciton-impurity complexes were first discussed by Lampert,<sup>2</sup> and luminescence due to the decay of four-particle complexes was first observed by Haynes,<sup>3</sup> who studied various donors and acceptors in Si. In both Si and SiC the transitions are indirect (phonon-assisted), resulting in series of lines from which phonon energies may be deduced. Edge emission due to three- and four-particle complexes has also been found in materials with direct transitions. A good reference is the recent paper on CdS by Thomas and Hopfield.<sup>4</sup>

In  $6H$  SiC, nitrogen substitutes for carbon equally on each of 3 inequivalent carbon sites,<sup>5</sup> resulting in 3

<sup>2</sup> M. A. Lampert, *Phys. Rev. Letters* **1**, 450 (1958).

<sup>3</sup> J. R. Haynes, *Phys. Rev. Letters* **4**, 361 (1960).

<sup>4</sup> D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **128**, 2135 (1962).

<sup>5</sup> Lyle Patrick, *Phys. Rev.* **127**, 1878 (1962).