in Statistical Physics, translated by R. A. Silverman (Prentice-Hall, Englewood Cliffs, N. J., 1963). See also C.-R. Hu and V. Korenman, Phys. Rev. 178, 684 (1969), and Ref. 22.

[29] We notice that Eqs. (6.1)–(6.3) are in fact identical to what is implied for the corresponding quantity in the vortex problem by the Eqs. (3)–(5) of Ref. 12 before the variable ρ is changed to x. We therefore suspect the existence of a transformation that could link the solutions of the two cases, but further study has yet to be made for a definite conclusion.

[30] Because of this we favor using the adjectives "unexpected" or "anomalous" rather than "nonanalytic" as is used by Jacobs (Ref. 12) to describe those terms in the expansion of BKJT free energy not predicted by the Ginzburg-Landau and Newmann-Tewordt theories.

[31] N. R. Werthamer, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Chap. 6.

[32] For the definitions of asymptotic expansion and the symbol '$\mathcal{O}$', see, for example, A. Erdelyi, *Asymptotic Expansions* (Dover, New York, 1956).

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Mössbauer Isomer Shifts in Sm^{149} Compounds

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The isomer shift (IS) of the 22.5-keV γ transition of Sm^{149} has been studied for various ionic, semiconducting, and metallic compounds using Mössbauer spectroscopy. We found changes as large as 0.9 mm/sec between trivalent and divalent compounds and 0.3 mm/sec between metallic and ionic trivalent compounds. The divalent compounds show a range of IS due to covalency effects, and the intermetallic compounds, which all have Sm in the trivalent state, show the extra electronic density due to the conduction electrons. The IS obtained for the semiconducting SmB_6, -0.4 mm/sec, and for the chalcogenide Sm_3S_4, -0.19 mm/sec, are anomalous. We calculated the difference in the mean-square charge radius between the 22.5-keV state and the ground state $\delta\langle r^2\rangle = 1.2\times10^{-3}$ fm^2. We also found the conduction-electron density at the nucleus of Sm metal $|\Psi|^2(\mathrm{CE}) = 0.95\times10^{26}$ cm^{-3}. The solid-state and nuclear results are discussed in the light of current theories.

INTRODUCTION

Isomer shifts (IS) in rare-earth nuclei have been observed during the past ten years, but relatively few measurements on IS of samarium compounds have been reported.[1] We have previously published the results[2] of measurements of the IS of SmB_6, and presented,[3] in abstract form, some results of IS measurements on divalent, trivalent, and intermetallic Sm compounds. This paper is the first extensive report of these measurements.

In particular, we present here measurements of the IS of Sm^{149} in various ionic, semiconducting, and metallic compounds, and determinations of the change of electronic density at the Sm nucleus due to chemical effects. The electronic structure of these materials is discussed in the light of the results. We have also determined the mean-square charge-radius change $\delta\langle r^2\rangle = \langle r_e^2\rangle - \langle r_g^2\rangle$ between the excited ($I=\frac{5}{2}$) and ground ($I=\frac{7}{2}$) states of Sm^{149} and will here compare the experimental value to that obtained from nuclear model calculations.

The shifts between centroids of Mössbauer spectra of various absorbers are usually described in terms of an electric monopole term, resulting from the electrostatic interaction energy between the nuclear charge density and the electronic density within the nuclear radius. This energy is different for different nuclear states, because of the effective nuclear charge-radius change $\delta\langle r^2\rangle$, and varies with effective electronic density, $|\Psi(0)|^2$, at the nucleus.[4,5]

The energy shift due to this interaction is given to a good accuracy by the formula[5,6]

$$\Delta E = E_1 - E_2 = \tfrac{2}{3}\pi\, Ze^2\left[\,|\Psi(0)|_1^2 - |\Psi(0)|_2^2\right]\delta\langle r^2\rangle\,, \qquad (1)$$

where E_1 and E_2 are the nuclear excitation energies in compounds with total electron density at the nucleus $|\Psi(0)|_1^2$ and $|\Psi(0)|_2^2$, and Z is the nuclear charge. The nuclear mean charge radii $\langle r^2\rangle_{e,g}$ in the excited state (e) and ground state (g) are defined by the relation

$$\langle r^2\rangle = \int \rho(r)\, r^2\, dr \Big/ \int \rho(r)\, dr\,, \qquad (2)$$

where $\rho(r)$ denotes the nuclear charge density, and the integral is taken over the nuclear volume. Relation (1) is exact to the first order, when the electron density is constant in the region of the nucleus[5,6] and relativistic electron densities are used.

EXPERIMENTAL

The Mössbauer absorption spectra were obtained in a standard transmission geometry, using a conventional constant-acceleration spectrometer.[7] The source used was Eu^{149}, made by (p, $2n$) reaction using a cyclotron. This particular approach is advantageous because if the Sm^{150}-separated isotope is used for the target, the isotopes produced by strong competing reactions are stable or very short lived, and the source contains no Sm^{149}, which would produce Mössbauer self-absorption. Thus, it was possible to use the Eu^{149} produced in the Sm_2O_3 matrix without a radiochemical separation. An irradiation of about 1400 μA h (done by the Oak Ridge Cyclotron) produced about 15 mCi of Eu^{149}; this gave a counting rate of about 2000 count/sec in the 22.5-keV γ-ray line. The source was used at room temperature, since lower temperatures produced substantial line broadening due to paramagnetic hyperfine structure (hfs).

The absorbers were polycrystalline samples of the materials studied containing Sm^{149} in natural abundance. The samples were immersed in a Dewar which could be filled with liquid helium, hydrogen, or nitrogen. The γ rays were detected by a silicon semiconductor detector, and counted using a multichannel analyzer running in the "time (multiscaler) mode." Some of the spectra were taken at room temperature and some spectra at low temperature. A few of the Mössbauer spectra obtained are shown in Figs. 1 and 2.

The methods of absorber preparation are described briefly below.

The chalcogenides SmS, SmSe, and SmTe were prepared by heating pressed pellets of prereacted[8] materials in evacuated and sealed tantalum crucibles at 1900, 1200, and 1750 °C for 2, 10, and 4 days, respectively, while Sm_2S_3 was heated similarly in a sealed tungsten crucible at 1800 °C for 2 h. The distorted perovskites, $SmAlO_3$, $SmFeO_3$, and $SmCrO_3$, were prepared using standard ceramic techniques. The intermetallic compounds $SmAl_2$ and $SmCu_2$ were prepared by mixing Sm and Al or Cu in stoichiometric proportion. The mixtures were melted in an inert-electrode arc furnace at an argon pressure of about 40 Torr and a temperature of about 1500 °C. The buttons were turned over and the materials were melted four times to ensure complete reaction. The $SmZn_2$ compound was prepared by mixing Sm and Zn in stoichiometric proportion and heating in an evacuated and sealed tantalum crucible for 3 h at 1200 °C. Sm_3S_4 was prepared by mixing Sm and S in stoichiometric proportion and heating in an evacuated and sealed silica tube for 5 days at 300 °C, then for 1 day at 600 °C, and for an additional day at 800 °C. The whole mixture was pressed into a pellet and after sealing in an evacuated Ta crucible was fired for 12 h at 1000 °C, then for 1 h at 1350 °C,

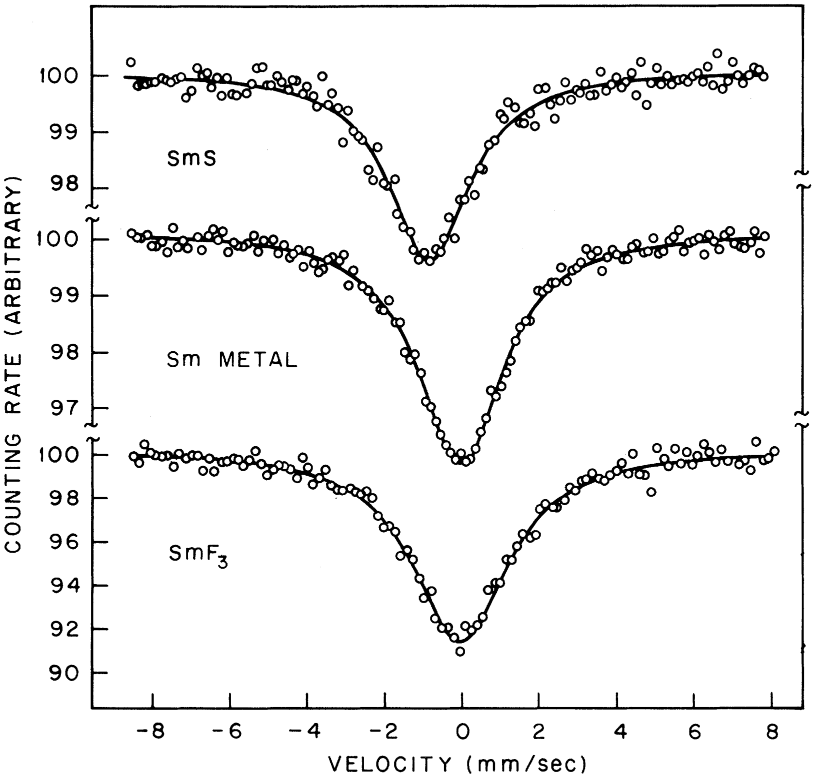

FIG. 1. Mössbauer spectra of SmS, Sm metal, and SmF_3 at room temperature. The solid line is a Lorentzian least-squares fit to the data.

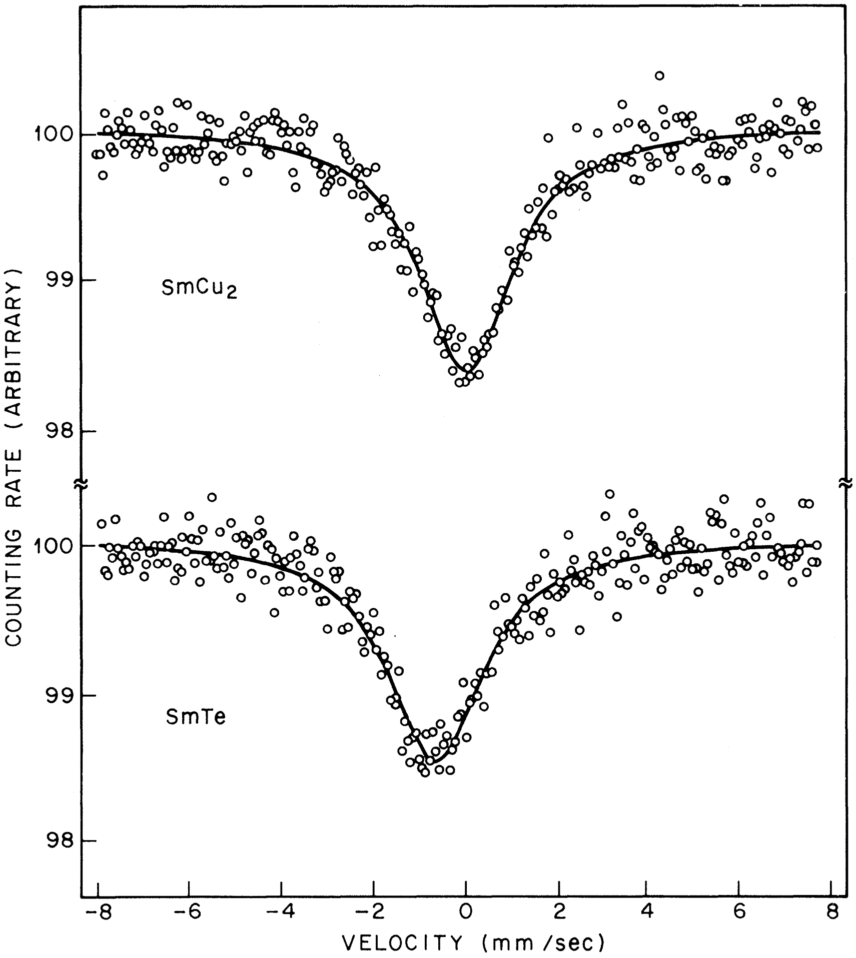

FIG. 2. Mössbauer spectra of $SmCu_2$ and SmTe at room temperature. The solid line is a Lorentzian least-squares fit to the data.

and finally for 1 h at 1700 °C. For the preparation of SmB_6 see Ref. 2. X-ray powder photographs were taken using a Norelco Straumanis camera with a diameter of 114.6 mm and Cr radiation. The patterns obtained showed only lines consistent with the known space groups of these materials.

The SmF_3 was prepared by heating the oxide with dry HF. The SmF_2 was prepared by heating SmF_3 with the stoichiometric amount of Sm metal in a sealed Ta crucible in vacuum. The material produced by this process fitted the description given in Ref. 9 for $SmF_{2.00}$. Over a few months, we discovered that the SmF_2 sample held in a sealed bottle gradually oxidized and turned red. The Mössbauer line of this red material was broad and shifted towards the Sm^{3+} isomer-shift value, verifying that oxidation had occurred.

The isomer-shift situation is complicated by the fact that the spectra of the trivalent compounds tend to broaden (because of paramagnetic hfs) at low temperature; this makes it desirable to measure the Sm^{3+} compounds at room temperature or 200 °K. The divalent compounds, however, can best be measured at low temperature because the paramagnetic hfs broadening of any trivalent contaminant reduces the effective intensity of the trivalent line. The experimentally observable energy shifts due to the isomer shift are superimposed on a term due to the second-order Doppler shift, which is temperature dependent. For this latter shift in Sm^{149} there is a high-temperature limiting value (for $T > \Theta_D$) of -0.03 mm sec^{-1} (per 100 °K) and a low-temperature limiting value of $9\Theta_D/16Mc$ ($= 0.01$ mm sec^{-1} at $\Theta_D = 100$ °K), M being the mass of the Sm nucleus. Most of the materials studied here have a Θ_D less than 300 °K, and we have therefore chosen to adjust all our results to 300 °K, since that makes it unnecessary to compensate for the different zero-point motion shifts.

RESULTS AND DATA ANALYSIS

The results of our measurements of IS of various samarium compounds relative to Sm_2O_3 source are shown in Fig. 3. The main results are that (a) the IS are very small, almost zero, among trivalent ionic Sm compounds. (b) In divalent compounds

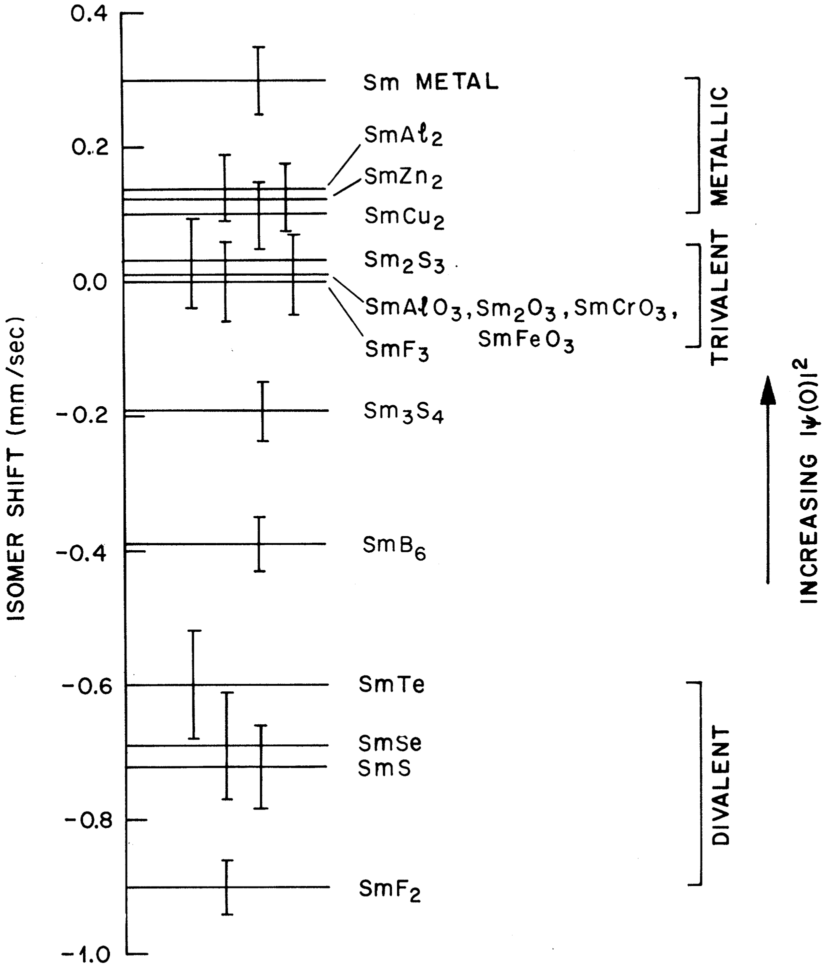

FIG. 3. Isomer shifts in Sm^{149} compounds and alloys at room temperature with respect to a $Sm:Eu_2O_3$ source at room temperature. Error flags have been conservatively chosen and include possible impurity effects as well as statistical errors.

the IS are appreciably shifted to smaller energies and exhibits a considerable spread of ΔE, with the most ionic compound SmF_2 showing the largest shift. (c) The IS for intermetallic compounds are shifted to higher energies and also exhibit a considerable spread of ΔE, but smaller than in the divalent compounds. The maximum IS was obtained for samurium metal $\Delta E = 0.3 \pm 0.06$ mm/sec. (d) The IS obtained for samarium hexaboride,[2] $\Delta E = -0.4$ mm/sec, and for the chalcogenide Sm_3S_4, $\Delta E = -0.19$ mm/sec are anomalous (see Fig. 3).

The shifts between divalent and trivalent ionic samarium compounds arise primarily from the change going from the electronic configuration $4f^6 5s^2 5p^6$ to $4f^5 5s^2 5p^6$. The difference in electron density at the nucleus exhibited by the IS between Sm^{3+} and Sm^{2+} is presumably produced by different shielding of the closed shell 5s electrons by the $4f^6$ and $4f^5$ configurations, i.e., the addition of one electron to the 4f shell increases the shielding of the 5s electrons and hence decreases the total electron density at the nucleus.

Two basic approaches have been used in the past to determine electronic charge-density changes in rare earths. Optical isotope-shift measurements in gases[10] yield $\Delta|\Psi^2|(EU^{3+} - Eu^{2+}) = 1.9 \times 10^{26}$ cm^{-3}; the corresponding value for Sm would be expected to be about 3% smaller. Hartree-Fock calculations for free ions yield a somewhat larger value,[11] $\Delta|\Psi^2|(Sm^{3+} - Sm^{2+}) = 2.85 \times 10^{26}$ cm^{-3}. More recent measurements confirm[12] these latter values, and suggest that the density changes in solids are not very different from the calculated free-ion values given above. We have therefore used the value $\Delta|\Psi^2|(Sm^{3+} - Sm^{2+}) = 2.85 \times 10^{26}$ cm^{-3} for the analysis and discussion below.

The isomer shift between the most ionic compounds studied, trivalent SmF_3 and divalent SmF_2, is 0.9 ± 0.1 mm/sec. If these compounds are assumed to be purely ionic and if the above indicated value for $\Delta\Psi^2(3^+ - 2^+)$ is taken, we calculate the difference in the mean-square charge radius between the 22.5-keV state and the ground state, using expression (1), to be $\delta\langle r^2\rangle = (1.2 \pm 0.1) \times 10^{-3}$ fm^2. Using the above value we also found the conduction-electron (CE) density at the nucleus of Sm metal $|\Psi|^2(\mathrm{CE}) = (0.96 \pm 0.15) \times 10^{26}$ cm^{-3}. This value is about 60% of the value reported by Henning *et al.*,[1] with the difference arising from slightly different isomer-shift value measured as well as from the slightly larger value of $\Delta\Psi^2(3^+ - 2^+) = 3.4 \times 10^{26}$ cm^{-3} used in their analysis.

The density $\Psi^2(0)$ of a 6*s* electron at the Sm nucleus is[5] 1.43×10^{26} cm^{-3} for a free atom. Thus, if the observed charge density difference of 0.95×10^{26} cm^{-3} between Sm metal and SmF_3 is attributed to CE of 6*s* character, the CE density corresponds to 0.66 of a free-atom 6*s* electron. Since there are three conduction electrons per Sm ion in the metal, this shows that the conduction band is primarily 5*d* in character. We have been able to find no band-structure calculations for Sm metal, but there have been a number of calculations for Gd and the heavy rare-earth metals,[13] which should have roughly similar band structures. Our result is consistent with these calculations. It is interesting to note that for all the rare-earth metals except Nd,[14] the ratio of the CE $\Psi^2(0)$ to the $\Psi^2(3^+ - 2^+)$ lies in the range 0.3 – 0.4. Since the latter term is roughly constant with the nuclear charge *Z*, this suggests that the CE $\Psi^2(0)$ is approximately 10^{26} cm^{-3} for all of those metals.

The electron density increases with ionicity for divalent chalcogenides (see Fig. 4). The increase of $|\Psi(0)|^2$ with the ionicity[15] may be attributed to bigger participation of 6*s* electrons in covalent bonds.[16] Covalency effects on the IS of Sm compounds seem similar to those observed in the corresponding Eu compounds.[17]

The measured IS of −0.19 mm/sec for Sm_3S_4 falls between the IS of Sm^{2+} and Sm^{3+}. This result could be explained using the "hopping model,"[18] with thermally excited electrons hopping from divalent to trivalent samarium ions producing both electrical conductivity and charge exchange between Sm^{2+} and Sm^{3+} ions.[19] All the Sm ions are in equivalent crystallographic sites,[20] which will allow this effect. The ratio of the two types of ions is 1:2 and then the IS is expected to be around[19] − 0.21 mm/sec which is in good agreement with that observed (− 0.19 ± 0.04 mm/sec).

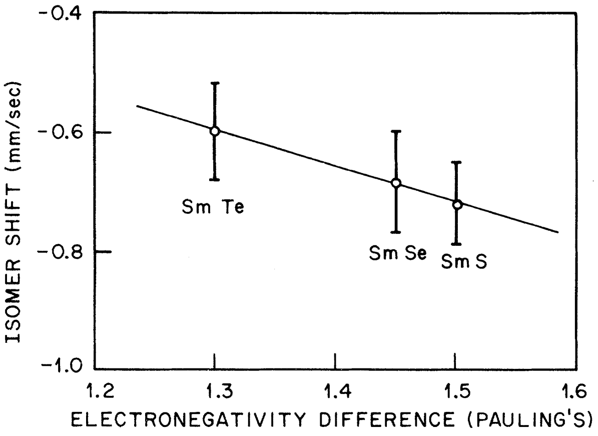

FIG. 4. Isomer shifts of divalent Sm chalogenides versus electronegativity difference between Sm and chalcogen.

TABLE I. Sm^{149} nuclear moments.

Measured	Neutron-core coupling model[a]	Nilsson model[b]
$\mu_e = (-0.618 \pm 0.001)\mu_N$[c]		$-0.33\mu_N$
$\mu_g = -0.665\mu_N$[d]		$-0.62\mu_N$
$\mu_e/\mu_g = 0.929$	0.86	
$Q_e = 0.50 \pm 0.05$ b[c]		(0.5 b)
$Q_g = 0.06 \pm 0.02$ b[c]		(0.06 b)

[a] Reference 22.

[b] With deformations adjusted to fit quadrupole moments, and core *g* factor of 0.2 (see D. A. Shirley, p. 1273 of Ref. 3, Vol. 4).

[c] Reference 3 (results here are consistent with those of Ref. 22, but of higher accuracy).

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The isomer shift and properties of SmB_6 have been discussed previously[2] in terms of a localized 5*d* electron bound to a $4f^5$ Sm core. This model has more recently been used[21] to discuss a variety of experimental measurements of SmB_6.

NUCLEAR SYSTEMATICS OF Sm^{149}

From the analysis of the observed hfs in Sm^{149}, we have previously[3] determined values for the nuclear moments of Sm^{149}. In Table I, these values are shown, together with theoretical estimates of the moments.

Nuclei in the region just below $A = 150$ have been difficult to model[21] because they seem to fit neither the shell nor collective models perfectly. The Sm^{149} nucleus is considered to lie at the beginning of the strongly deformed region; Sm^{148} is not strongly deformed, while Sm^{150} is at least somewhat deformed. Ofer and Nowik[22] have previously shown that the Sm^{149} states could be described by considering the ground state as a $\frac{7}{2}$ neutron orbital and the 22.5-keV state as this same neutron orbital coupled to a 2^+ collective core excitation, to produce $I = \frac{5}{2}$. This approach reproduces the observed ratio of μ_e/μ_g (see Table I) if a simple angular-momentum-vector coupling argument is used to combine the core and odd-neutron moments.

The 0.5-b quadrupole moment[23] of the 22.5-keV state is rather large to arise from an odd-neutron orbital alone (Nd^{143} is the only other nondeformed nucleus with a quadrupole moment that large in this region), and it is interesting to see if the Sm^{149} states can be analyzed in terms of the Nilsson model, with a relatively small core deformation.[24] There are in fact odd-neutron orbitals of the proper spin and parity available at the "low-deformation" end of the energy-level diagram. Using a $\frac{7}{2}^-$[514] orbital (with deformation parameter $\beta = 0.01$ for the ground state) and a $\frac{5}{2}^-$[523] orbital (with $\beta = 0.07$, to produce the observed quadrupole moment) the magnetic moments of the ground and 22.5-keV states can be calculated, and are shown in Table I. They are in fair agreement with the observed values, considering the small absolute size of the moments and the fact that no parametric adjustment has been made. The higher-energy states of Sm^{149} could also be readily understood with this approach: There are no states in the region from 22 to 280 keV, at which energy there is then a doublet. This could arise from the odd-neutron orbitals we have mentioned above, plus a core excitation.

For both Dy^{161} [25] and Yb^{171} [26] it has been shown that simple phenomenological approaches to the calculation of $\delta\langle r^2\rangle$ is deformed nuclei tend to be unsuccessful. More complex calculations, by Speth[27] based on the Migdal-Larkin theory, have had some success, but have not been performed for Sm^{149} so far as we know. So there is at present no satisfactory theory to account for our measured $\delta\langle r^2\rangle$.

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