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Isotopic Shift in the Electron-Spin-Resonance Absorption Spectrum of Gd^{3+} in Thorium Oxide*

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The fine-structure spectrum of trivalent gadolinium occurring as a cation substitution in thorium oxide has been reinvestigated to determine whether this crystal-ion system exhibits fine-structure splittings which are dependent upon isotopic species. Such a dependence has been observed; however, the magnitude of the effect is found to be just within the limits of detectability. For this crystal-ion system, three spin-Hamiltonian parameters are found to be sufficient to characterize the fine-structure spectrum, an isotopic g value, and two crystal-field-splitting energy parameters, b_4 and b_6. At 77°K the relative shift in b_4 between ^{155}Gd and ^{157}Gd is $\delta b_4/b_4=4.2\times10^{-5}$, the value of b_4 associated with the heavier isotope being greater in magnitude. No shifts in the g value or in b_6 could be detected. When differences in the fine-structure parameter b_4 are measured using the average spectral component positions due to the $I=0$ isotopes as references, shifts for ^{155}Gd and ^{157}Gd are obtained which follow a simple mass-difference-ratio relationship.

I. INTRODUCTION

WHENEVER a crystal-ion system exhibits relatively narrow electron-spin-resonance (ESR) linewidths, generally of the order of an oersted or less, opportunities become available for making precise spectral measurements and for obtaining spectroscopic information not otherwise available. In particular, a detailed investigation of a crystal-ion system exhibiting narrow components may prove useful in establishing the validity of using a particular energy operator for a spectral description or for establishing the appropriate form of this operator.

Trivalent gadolinium located as a cation substitution in single-crystal thorium oxide exhibits an ESR absorption spectrum which for more than one reason makes it attractive as a subject for such a study.[1–3] To begin with, the spectrum appears to be locally cubic which is a symmetry for which the application of group theory is relatively uncomplicated.[4] In strong Zeeman fields, the spectrum consists of seven $\Delta M_s=\pm1$ transitions, three of which may in principle be used to solve for the three fine-structure parameters required by the conventional spin Hamiltonian.[5,6] The remaining four transitions may then be used as checks on the degree of adequacy of a three-parameter energy operator.[7,8] Another aspect of this spectrum is its hyperfine structure which arises from the two isotopes ^{155}Gd and ^{157}Gd of natural abundances 14.78 and 15.71%, respectively, both of which have nuclear-spin quantum numbers $I=\frac{3}{2}$, with nuclear magnetic moments sufficiently different to allow all their M_I spectral components to be resolved for at least one of the seven fine-structure transitions (see Fig. 1). There are an additional five isotopes of gadolinium which have zero nuclear spin, the three most abundant being ^{156}Gd, ^{158}Gd, and ^{160}Gd whose natural abundances are 20.59, 24.78, and 21.79%, respectively.[9] Such a collection of isotopic species, that is, at least two distinct species having nonzero nuclear spin and two or more zero-spin species of comparable natural abundances, represents a favorable set of conditions for conducting a search for

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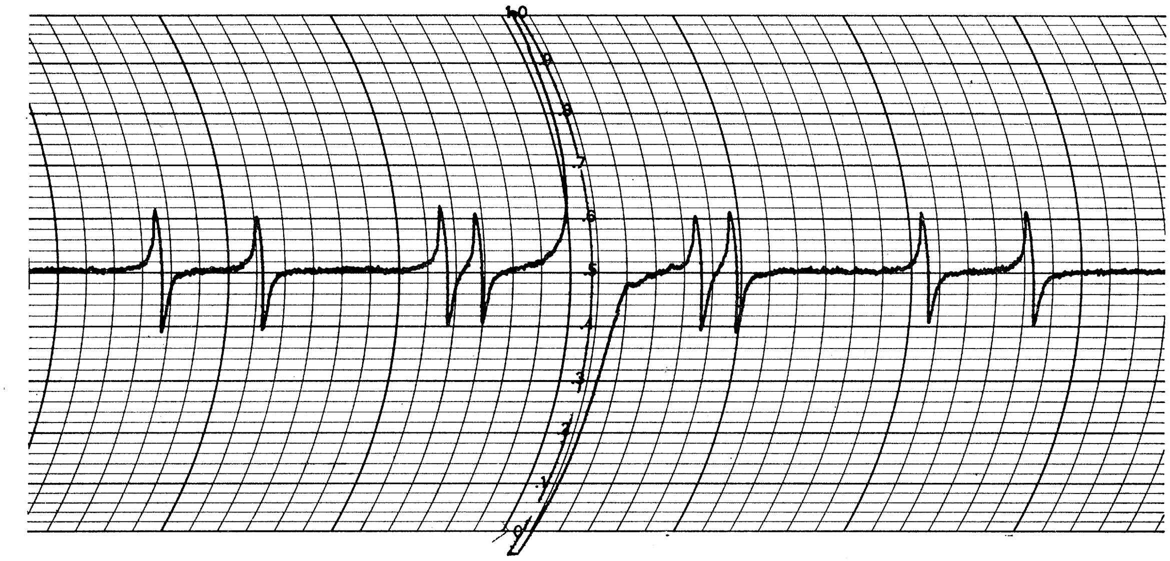

FIG. 1. First-derivative tracing of the $M_s = -\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition of trivalent gadolinium taken at 77°K.

a fine-structure spectral dependence on isotopic species.[10,11] The object of a search of this nature would first of all be to determine the existence of the effect as well as its dependence upon temperature for an ion of the rare-earth series and having done this, to determine whether the effect is dependent upon isotopic mass or upon the magnetic moment of the nucleus.

In this report, the results of such an investigation carried out on the spectrum of trivalent gadolinium located as a cation substitution in single-crystal thorium oxide are presented. These results demonstrate that an isotopic shift does exist and that although the shifts are quite small, just within the experimental limits of detectability, a specific mass-difference ratio does exist which is roughly 3:1, as might be expected.

II. EXPERIMENTAL PROCEDURE

Single-crystal thorium oxide specimens containing less than ten parts per million of gadolinium were used in this study. The specimens, grown by the Norton Company, varied in their ability to transmit visible radiation from opaque to translucent, displayed an amber coloration, and exhibited relatively narrow trivalent gadolinium resonance absorption linewidths (see Table I). The crystals having the fluorite structure cleave readily in {111} planes so that orienting and mounting presented no particular difficulty. Octahedral fragments of about 0.3 cm to an edge were mounted on fused silica pedestals having a face cut so as to enable the Zeeman field to be rotated in either a {110} or {100} plane of the crystal. Pedestal and specimen were placed along the symmetry axis of a cylindrical cavity resonator operating in the TE_{011} mode with a loaded Q of the order of 5000. A 3-cm-wavelength spectrometer was used having a 30-Mc/sec superheterodyne detector to allow operation at power levels which varied from 10^{-7} to 10^{-9} W depending upon the temperature of the specimen.

Special precautions were exercised in making the spectral observations to avoid such difficulties as (a) orientation uncertainties, (b) spurious line broadening due to power saturation and overmodulation of the Zeeman field, (c) uncertainties in determining peak position of the absorption lines, (d) drift of the signal oscillator frequency, and (e) artifically induced asymmetries in the resonance absorption line shapes. Preliminary orientation was established by mounting a cleaved specimen on a specially cut pedestal. The next step was to establish *in situ*, those spectral-line extrema field positions associated with specific crystallographic directions. Finally, the spectrum of what is believed to be due to iron located at sites having {111} distortions was used as a fine adjustment of the orientation. This adjustment was found to be quite critical since along a

TABLE I. Trivalent gadolinium resonance absorption linewidths[a] given in oersteds for the Zeeman field directed along a cube edge taken at various temperatures.

Transition	4.2°K	20°K	59°K	77°K
$\pm\frac{5}{2} \leftrightarrow \pm\frac{7}{2}$	1.10	0.97	0.61	0.81
$\pm\frac{3}{2} \leftrightarrow \pm\frac{5}{2}$	0.80	0.58	0.45	0.62
$\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$	0.72	0.50	0.35	0.53
$-\frac{1}{2} \leftrightarrow \frac{1}{2}$	0.53	0.30	0.12	0.18

[a] Errors in linewidth measurements estimated at ±10%.

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cube edge four spectral components (one due to each of four inequivalent {111} directions) superimpose at a nonextremum field-strength position. Absorption-line peak field positions were obtained by stabilizing the Zeeman field on the peak of an absorption through the use of a phase-sensitive lock-in type detector network whose dc output was fed into the control circuit of the electromagnet current supply. With the Zeeman field locked to the absorption peak, its strength was measured with a proton magnetometer. For a given fine-structure transition, the field strengths of the hyperfine quartets due to ^{155}Gd and ^{157}Gd were determined as was the one component due to the even isotopes of gadolinium, while the frequency of the signal oscillator was monitored. It was found that in the time taken to make such a set of measurements the signal oscillator frequency did not drift by more than 10 kc/sec. Before making a set of measurements, the resonance absorptions were checked for line-shape symmetry. This was usually done by inspecting one of the four $M_I=\pm\frac{3}{2}$ hyperfine components of the $M_s=-\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition which were well resolved. Finally, measurements were made at the lowest possible microwave power and Zeeman-field modulation levels necessary to ensure minimum interference from wings of neighboring spectral components.

III. RESULTS AND CONCLUSIONS

Trivalent gadolinium incorporated in the thorium oxide lattice exhibits an ESR absorption spectrum having cubic symmetry which displays greatest component separations when the Zeeman field is directed along a cube edge. For an ^{8}S ion located at the site of body-centered cubic symmetry, the following spin Hamiltonian may be used in analyzing the spectrum

$$\mathcal{H}=\left.\begin{array}{l} g\beta HS_z+g^n\beta^nHI_z+\tilde{A}\mathbf{I}\cdot\mathbf{S} \\ \quad +\tilde{b}_4[Y_4^0-5(Y_4^4+Y_4^{-4})] \\ \quad +\tilde{b}_6[Y_6^0+21(Y_6^4+Y_6^{-4})] \end{array}\right\}\text{(a)}$$
$$\left.\begin{array}{r} +\tilde{B}[4IS(2I-1)(2S-1)]^{-1} \\ \times[3I_z^2-I(I+1)] \\ \times[3S_z^2-S(S+1)] \\ +\tilde{C}I_zS_z^3, \end{array}\right\}\text{(b)} \qquad (1)$$

where the Y_n^m are electron-spin operator polynomials of degree n having m-fold rotation symmetry and the remaining terms in section (a) have their conventional spectroscopic meaning.[12] The two less familiar terms in section (b) are truncated operators which arise from higher-order perturbations of the form which involve the interactions $\tilde{A}\mathbf{I}\cdot\mathbf{S}$.[8,9,13–16] In the absence of hyperfine interaction, the eigenvalues to this energy operator evaluated within the $S=\frac{7}{2}$ manifold may be obtained from the following expressions:

$$E_1=\tfrac{3}{2}H+(8b_4-2b_6)\pm 2H[1-\tfrac{1}{3}\alpha+\alpha^2]^{1/2},$$
$$E_2=\tfrac{1}{2}H-(8b_4-2b_6)\pm 2H[1-\beta+\beta^2]^{1/2}, \qquad (2)$$

where the substitutions $b_4=\tilde{b}_4/g\beta$, $b_6=\tilde{b}_6/g\beta$, $\alpha=(3b_4-9b_6)/H$, and $\beta=(5b_4+7b_6)/H$ are made. These two expressions provide all eight eigenvalues (in units of magnetic field), four by alternation of the sign before the radical and four more by substitution of $-H$ for H. Although these two expressions are not overly complex, a great aid to spectral-parameter calculation may be achieved in the region of strong Zeeman field strengths by expanding the radicals to obtain approximate but rational eigenvalue expressions which are given by

$$E(\pm\tfrac{7}{2})=\pm\tfrac{7}{2}H+(7b_4+b_6)\pm[\tfrac{35}{36}\alpha^2\pm\tfrac{35}{216}\alpha^3-\tfrac{2165}{5184}\alpha^4],$$
$$E(\pm\tfrac{5}{2})=\pm\tfrac{5}{2}H-(13b_4+5b_6)\pm[\tfrac{3}{4}\beta^2\pm\tfrac{3}{8}\beta^3+\tfrac{3}{64}\beta^4],$$
$$E(\pm\tfrac{3}{2})=\pm\tfrac{3}{2}H-(3b_4-9b_6)\pm[\tfrac{3}{4}\beta^2\mp\tfrac{3}{8}\beta^3+\tfrac{3}{64}\beta^4],$$
$$E(\pm\tfrac{1}{2})=\pm\tfrac{1}{2}H+(9b_4-5b_6)\pm[\tfrac{35}{36}\alpha^2\mp\tfrac{35}{216}\alpha^3-\tfrac{2165}{5184}\alpha^4]. \qquad (3)$$

In reducing experimental fine-structure data it becomes evident from an inspection of Eq. (3) that some labor is saved by using two sets of conjugate transitions[17] to obtain the fine-structure spectral parameters. The four transitions $M_s=\pm\frac{3}{2}\leftrightarrow\pm\frac{5}{2}$ and $M_s=\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ were used for this purpose, while the three transitions $M_s=-\frac{1}{2}\leftrightarrow\frac{1}{2}$ and $M_s=\pm\frac{5}{2}\leftrightarrow\pm\frac{7}{2}$ were used as consistency tests of the spectral-parameter determinations. The degree to which this consistency is attained as well as the adequacy of the energy operator given by Eq. (1), at a given wavelength, is determined by how well the calculated field-strength positions of the three test transitions agree with observations. Considering the widths of the resonance absorption lines, no set of data was considered acceptable unless the foregoing agreement was found on the average to be within ±0.2 Oe. In addition, applying this test to establish the adequacy of the approximate eigenvalue expressions, the spin-Hamiltonian fine-structure parameters were determined from 4.2 to 294°K in temperature intervals of about 30°K. The only parameter that exhibited a measurable dependence on temperature was b_4 (see Fig. 2 and Table II).

Hyperfine-structure interaction may be incorporated into the calculations through the operators AI_zS_z and

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[17] In this context, two transitions are defined to be conjugate if their respective m_s quantum numbers differ only in sign.

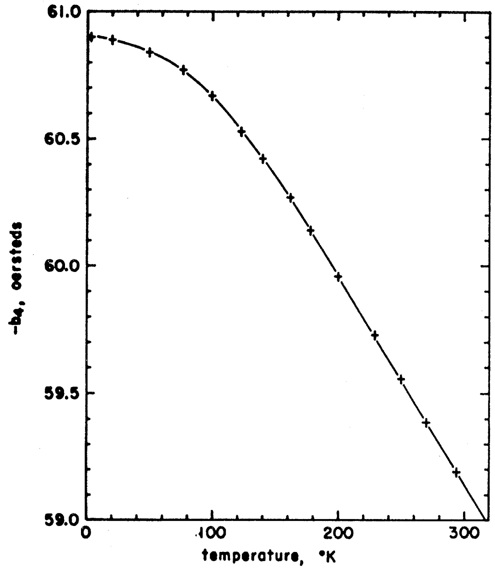

FIG. 2. Temperature dependence of the fourth-order cubic-field splitting parameter b_4 taken from 4.2°K to room temperature.

$\frac{1}{2}A[I_+S_-+I_-S_+]$, $A=\tilde{A}/g\beta$, the latter operator connecting states $|M_s, M_I\rangle$ with $|M_s\pm1, M_I\mp1\rangle$, where M_s and M_I are electron- and nuclear-spin quantum numbers, respectively. In addition, the higher-order hyperfine interactions may be accounted for by the approximate expressions given in section (b) of Eq. (1). Because of the manner in which the abundances, angular momenta, and magnetic moments of the stable gadolinium nuclei occur in nature, each fine-structure transition appears as a nonet, four components due to ^{155}Gd, another four due to ^{157}Gd, and one due to the remaining $I=0$ isotopes. Since the Zeeman-field positions of the spectral components due to $I=0$ isotopes require no hyperfine-structure corrections, the field positions of these spectral components may be conveniently used as fiduciaries in determining spectral displacements of the nonzero-spin isotopes. As a result of the way in which the natural abundances of the three most abundant $I=0$ isotopes of gadolinium occur, it is felt that a nuclear-mass-dependent fine-structure spectral shift between these would produce very little resonance absorption line shape asymmetry, since the difference in natural abundance between ^{156}Gd and ^{160}Gd amounts to only 1.20%, each being two mass units displaced from ^{158}Gd, one to either side. It would thus appear that a mass-dependent shift between the fine-structure spectra associated with the three most abundant $I=0$ isotopes would result in a single spectrum of nearly symmetric components. Whether or not such a shift occurs in the $I=0$ spectra, it is concluded that the unresolved components may be used as fiduciaries and identified with the ^{158}Gd isotope.

TABLE II. Parameters to the spin Hamiltonian determined at 77°K.

Quantity	Value
g	$[1.99161\pm0.00003]$
b_4	$[-60.770\pm0.010]$ Oe
b_6	$[-0.438\pm0.001]$ Oe
^{155}A	$[-4.327\pm0.003]$ Oe[a]
^{157}A	$[-5.673\pm0.003]$ Oe[a]
$[^{157}b_4-{}^{155}b_4]/b_4$	4.2×10^{-5}
$^{155}A/^{157}A$	$[0.7628\pm0.0008]$[a]
^{157}B	$[-0.246\pm0.007]$ Oe[b]
^{157}C	$[-0.0036\pm0.0013]$ Oe[b]

[a] Determined from the $M_s=-\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition.
[b] See Ref. 16.

TABLE III. Averages of the fine-structure spectral position shifts and hyperfine-structure parameters given in oersteds and taken at 77°K.[a]

Transition	$^{155}\Delta$	$^{157}\Delta$	^{155}A	^{155}A
$-\frac{3}{2}\leftrightarrow-\frac{1}{2}$	0.035	0.011	−4.325	−5.674
$-\frac{5}{2}\leftrightarrow-\frac{3}{2}$	0.040	0.010	−4.336	−5.685
$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0.001	0.001	−4.327	−5.673
$\frac{3}{2}\leftrightarrow\frac{5}{2}$	−0.042	−0.015	−4.333	−5.691
$\frac{1}{2}\leftrightarrow\frac{3}{2}$	−0.031	−0.011	−4.324	−5.664

[a] Uncertainties in Δ and A are estimated at ±0.003. Δ is defined as the corrected difference in effective fine-structure Zeeman-field-strength positions between the zero- and nonzero-spin isotopes. Corrections involved in determining $^{155}\Delta$ and ^{155}A were obtained from estimates to the spectral parameters B and C for ^{155}Gd based upon ^{157}Gd data (Refs. 13 and 16).

Fine-structure spectral shifts were analyzed for five electron-spin transitions with data taken on only the $M_I=\pm\frac{3}{2}$ hyperfine-structure components, since these were the best resolved for all transitions. Typical results taken at 77°K are summarized in Table III. To interpret these results, reference is made to the approximate eigenvalue expression given by Eq. (3) which may be further simplified by neglecting contributions made by α and β. Transition-field-strength positions so obtained are given by

$$\begin{aligned}
H(\pm\tfrac{5}{2}\leftrightarrow\pm\tfrac{7}{2})&=H_0\mp(20b_4+6b_6),\\
H(\pm\tfrac{3}{2}\leftrightarrow\pm\tfrac{5}{2})&=H_0\pm(10b_4+14b_6),\\
H(\pm\tfrac{1}{2}\leftrightarrow\pm\tfrac{3}{2})&=H_0\pm(12b_4-14b_6),\\
H(-\tfrac{1}{2}\leftrightarrow\tfrac{1}{2})&=H_0,
\end{aligned}\tag{4}$$

where $H_0=h\nu/g\beta$. The first fine-structure parameter to be considered is the spectroscopic splitting factor. In first order, this parameter determines H_0 so that its isotopic dependence should be most unambiguously determined from the $M_s=-\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition. Upon taking second-order field-strength corrections into account which arise from the off-diagonal hyperfine-structure operator, no measurable shift was observed for this parameter. (The uncertainty quoted in Table II for the g value is an absolute rather than a relative quantity resulting principally from the fact that the Zeeman-field-strength measuring probe was physically displaced from the specimen being studied.) Any shifts in the field-strength positions of the remaining transitions may now be interpreted as due to shifts in the parameters b_4 and b_6. (The $M_s=\pm\frac{5}{2}\leftrightarrow\pm\frac{7}{2}$ transitions were not used in the isotope-shift analysis because of excessive linewidths.) As a consequence of the alternating signs before the fine-structure contributions of conjugate transitions [see Eq. (4)] shifts may be checked by comparing magnitudes and relative signs between two such transitions. From the summary given in Table III it can be seen that, to within experimental error, the two transitions $M_s=\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ exhibit corrected shifts which are of equal magnitude and opposite sign, while the two transitions $M_s=\pm\frac{3}{2}\leftrightarrow\pm\frac{5}{2}$ exhibit a similar sign alternation relationship with shifts of roughly the same magnitude. Considering the quoted probable error, this agreement as well as the absence of a measurable shift for the $M_s=-\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition is taken as evidence for a very small but definite isotopic shift in the fine-structure parameter b_4.

An attempt at extending these measurements to other temperatures encountered problems associated with excessive linewidths. The data given in Table I give an indication of this difficulty. It will be seen that at temperatures below 50°K, all the spectral components exhibit an anomalous broadening despite the fact that precautions were taken to avoid power saturation. At 4.2 and 20°K, for example, measurements were made at power levels of the order of 10^{-9} W. Results on isotopic shift were obtained at 50 and 200°K. At the former temperature, the isotopic-shift results appear to be about the same as those obtained at 77°K, while at the latter temperature the shifts measure to be about one-half those at 77°K.

In conclusion, it may be said that as expected, an isotopic shift has been observed in the fine-structure spectrum of trivalent gadolinium located at the thorium-ion sites of thorium oxide. The effect is, however, quite small (an order of magnitude or so below the same effect observed in the spectra of trivalent iron and chromium located at the octahedral sites of calcite and periclase, respectively). As in the case of the trivalent chromium-periclase system, the isotopic shift exhibits a temperature dependence which decreases in magnitude as temperature is raised. This seems to be in keeping with the phenomenological expression given in Ref. 11 which relates the isotopic shift of a fine-structure parameter with the temperature dependence of the parameter itself and the isotopic-mass change

$$\delta\langle b_4\rangle/b_4^0\cong-\tfrac{1}{2}\{(\langle b_4\rangle-b_4^0)/b_4^0\}(\delta M/M), \qquad (5)$$

where $\langle b_4\rangle$ is a mean value of b_4 obtained through a procedure outlined in Ref. 11, and b_4^0 is the hypothetical value b_4 would have taken on if the lattice were rigid. In the present case, the value of $\langle b_4\rangle$ diminishes in magnitude as temperature increases; however, the average mass of the $I=0$ isotopes is greater than either of the two $I=\frac{3}{2}$ isotopes so that a fine-structure shift whose magnitude diminishes with temperature does not seem to be at variance with the trivalent chromium-periclase results. Equation (5) also predicts that the isotope shift should be proportional to the nuclear mass change. An examination of Table III reveals that the shift for ^{155}Gd is indeed greater than that for ^{157}Gd, and by a factor of approximately 3 as the equation suggests.

Finally, two supplementary results have been obtained as byproducts of this investigation. The first deals with the adequacy of a three-parameter energy operator in describing this fine-structure spectrum at a given wavelength. As previously stated, the test of this adequacy is the ability of such an operator to predict spectral positions to within an accuracy of, say, one linewidth. At the wavelength of 3 cm and for this crystal-ion system, the tests were very well met at various temperatures but only after proper orientation precautions had been taken. The second supplementary result is the determination of the sign of the hyperfine-structure parameter with reference to the sign of the cubic electric-field splittings. With $S>\frac{1}{2}$, the sign of A may be determined through the influence of second-order perturbations on the magnitude of A and for this system, scatter in the value of this parameter was determined to be greater by a factor of 6 for $A>0$ than for $A<0$.

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