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Author

Edelstein, N.

Publication Date

1979-03-01

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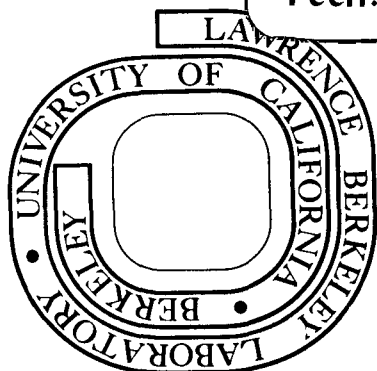
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March 1979

Prepared for the U. S. Department of Energy
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Comment on the Electron Paramagnetic Resonance Spectrum
of the Γ_8 Ground State of Np^{4+} Diluted in Cs_2ZrCl_6

N. Edelstein, W. Kolbe,^{*} and J. E. Bray[†]

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

March 1979

ABSTRACT

The electron paramagnetic resonance spectrum of Np^{4+} diluted in CsZrCl_6 is analyzed in terms of the theory formulated by Belorizky, et al. It is shown that if g_J , the Lande g factor is allowed to vary freely, a satisfactory fit may be obtained which is consistent with optical and epr data obtained earlier on other tetrapositive actinide ions in the same host crystal. It is suggested a better fit between the experimental data and the calculated spectrum may be obtained if the Zeeman mixing between the ground Γ_8 state and the excited Γ_6 state is considered.

^{*}Associated with the Engineering and Technical Services Division, Lawrence Berkeley Laboratory.

[†]Permanent address: Dept. of Physics, Marietta College, Marietta, OH 45750.

Introduction

Optical and electron paramagnetic resonance (epr) spectra of Np^{4+} in crystals of Cs_2NpCl_6 and Cs_2ZrCl_6 show the metal ion to be at a site of octahedral symmetry with a Γ_8 ground state.¹ Lea, Leask, and Wolf (LLW),² among others, have shown that the measured g values obtained from the epr spectra of the Γ_8 state for $J = 9/2$ are dependent upon the ratio of the fourth and sixth order crystal field parameters. From a qualitative interpretation of the epr spectrum of the Γ_8 state of Np^{4+} diluted in Cs_2ZrCl_6 , Bray concluded that the LLW parameter x (a measure of the above ratio) was equal to -0.567 which is in contradiction to the value expected for an octahedral complex and found for other actinide ions (See Table 1). In this paper we reanalyze quantitatively the epr spectrum of $^{237}\text{Np}^{4+}$ diluted in single crystals of Cs_2ZrCl_6 and show that the LLW parameter x has a positive value as expected for octahedral symmetry.

Review of Theory

The ground term of $\text{Np}^{4+}(5f^3)$ is nominally $^4I_{9/2}$. Although crystal field interactions in the actinide series are larger than in the 4f series, we assume we are dealing with an isolated J level; that is there is no J mixing by the crystal field. We later take into account the effects of spin-orbit coupling and other interactions which may change the free ion Lande g value, g_J , by allowing this parameter to vary. The

representation $D^{9/2}$ reduces under O_h symmetry to two Γ_8 and one Γ_6 representations. Since there are two Γ_8 representations the relative eigenvalues and eigenvectors of these levels depend on the ratio of the fourth and sixth order crystal field parameters. Lea, Leask, and Wolf² have calculated these eigenvalues and eigenvectors for $J = 1/2$ to $15/2$ as a function of the parameter x (see below).

The crystal field Hamiltonian for O_h symmetry may be written as^{3,4}

$$\mathcal{H}_C = A_4 \langle r^4 \rangle \beta [O_4^0 + 5O_4^4] + A_6 \langle r^6 \rangle \gamma [O_6^0 - 21O_6^4]$$

where $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ are the fourth and sixth order crystal field parameters respectively, β and γ are the fourth and sixth order operator equivalent factors, and the O_k^q are the equivalent tensor operators. The matrix elements of the O_k^q and the operator equivalent factors have been tabulated for the ground terms of all J states of the f^n ions. Lea, Leask, and Wolf^{2,4} defined the parameter x as

$$\frac{x}{1-|x|} = \frac{F(4)A_4 \langle r^4 \rangle \beta}{F(6)A_6 \langle r^6 \rangle \gamma}$$

The relative energy levels and eigenfunctions have been calculated for all ratios of the crystal field parameters as x varies from $x = -1$ to 0 to $+1$. The constants $F(4)$ and $F(6)$ are tabulated multiplicative factors for particular J states for the matrix elements of the fourth and sixth order

operators. Figure 1 shows the relative energy levels of the $J = 9/2$ state for octahedral symmetry as a function of x . We see that for $x \lesssim .83$ the $\Gamma_8^{(2)}$ state will be lowest and for $x \gtrsim .83$ the Γ_6 state will be the ground state.

The eigenvectors of the fourfold degenerate $\Gamma_8^{(2)}$ state for a $J = 9/2$ multiplet with the axes chosen as the principal axes of an octahedron may be divided into two pairs

$$A : a_1 |\pm 9/2\rangle + a_2 |\pm 1/2\rangle + a_3 |\mp 7/2\rangle$$

$$B : b_1 |\pm 5/2\rangle + b_2 |\mp 3/2\rangle$$

where the quantum numbers inside the kets correspond to $|J_z\rangle$ values for the $J = 9/2$ state and the a_i and b_i depend on the value of x . These eigenvectors may also be labeled as $|\Gamma_8^{(2)} \pm 1/2\rangle$ and $|\Gamma_8^{(2)} \pm 3/2\rangle$ where the $\pm 1/2$ and $\pm 3/2$ are eigenvalues of an operator \tilde{J}_z where \tilde{J}_z is equal to the usual J_z operator for the representation $J = 3/2$ ($\Gamma_8 \subset D^{3/2}$). Ayant, et al.⁵ have shown that with the above basis vectors the J_z submatrix for the fourfold degenerate Γ_8 states of $J = 9/2$ may be written as

$$J_z = \begin{vmatrix} P & & & \\ & Q & & \\ & & -Q & \\ & & & -P \end{vmatrix}$$

with $P = \langle \Gamma_8^{(2)} 3/2 | J_z | \Gamma_8^{(2)} 3/2 \rangle$ and $Q = \langle \Gamma_8^{(2)} 1/2 | J_z | \Gamma_8^{(2)} 1/2 \rangle$

where we have now labeled the pairs A and B as

$$|\Gamma_8^{(2)} \pm 1/2\rangle \text{ and } |\Gamma_8^{(2)} \pm 3/2\rangle.$$

If we consider the magnetic resonance spectrum with the magnetic field along the 001 direction, then

$$h\nu = 2g_J P \beta' H \quad \text{and} \quad h\nu = 2g_J Q \beta' H$$

for the two components of the $\Gamma_8^{(2)}$ state where β' is the Bohr magneton and H is the magnitude of the applied magnetic field. From the epr data of Bray¹ taken in the 110 plane it is clear that H will be very large for the 001 direction and therefore Q must be near zero. Figure 2 shows a plot of the values of P and Q for the $\Gamma_8^{(2)}$ state as a function of x . There are two ranges of x for which Q is near zero, $x \sim -.60$ and $x \sim .65$. Bray chose to fix g_J , the free ion g value for the $J = 9/2$ state, at the value calculated by Menzel and Gruber⁶ in their study of the optical spectrum of Cs_2NpCl_6 and found he qualitatively obtained the best fit at $x = -.567$. We have allowed g_J to be a free parameter in our fitting procedure and find the epr data can be fitted with a positive x value in agreement with the optical data of other tetrapositive actinide ions in octahedral host crystals as shown in Table 1. In fact the x values obtained for Pa^{4+} and U^{4+} in Cs_2ZrCl_6 suggest we are near the crossover point for the Γ_6 and $\Gamma_8^{(2)}$ states. The observation of the $\Gamma_8^{(2)}$ epr resonances with no indication at $\sim 1.5^\circ\text{K}$ of an isotropic epr Γ_6 resonance shows that $x < .83$.

The isotope ^{237}Np possesses a large nuclear magnetic moment of spin $I = 5/2$. The theory of the electron paramagnetic resonance (epr) spectrum of a Γ_8 state with hyperfine

structure has been worked out by Belorizky, Ayant, Decampes, and d'Aubigné⁷ to various levels of approximation depending on the relative magnitude of the hyperfine coupling interaction to the Zeeman interaction. In the present case we used the Hamiltonian as given by Belorisky, et al.⁷

$$\mathcal{H} = g_J \beta \vec{H} \cdot \vec{J} + A \vec{I} \cdot \vec{J} + B [(\vec{I} \cdot \vec{J})^2 + 1/2(\vec{I} \cdot \vec{J}) - 1/3(\vec{I}^2 \vec{J}^2)] \quad , \quad (1)$$

calculated the matrix elements and diagonalized and the resulting matrix. The first term in the Hamiltonian is the Zeeman interaction, the second term the hyperfine interaction, and the third term the quadrupole interaction. The hyperfine coupling constant A, and the quadrupole coupling constant B, are both in energy units. The above Hamiltonian is similar to that used in atomic spectroscopy for the Zeeman effect in free atoms whose nuclei have spin $I > 1/2$. The theory and the necessary matrix elements are given in Ramsey's book.⁸

A computer program was written which calculated the matrix elements of the Hamiltonian of Eq. (1) in the $|JJ_z II_z\rangle$ representation. This matrix was complex and of rank 24; a fourfold degeneracy arising from the electronic Γ_8 state and a sixfold degeneracy from the nuclear spin, $I = 5/2$. The magnetic field can be in an arbitrary but known direction and the vector quantity was broken up into components along the octahedral axes of the crystal.

For a particular magnetic field and a particular set of Γ_8 wavefunctions (corresponding to a unique x value) the matrix elements of the Hamiltonian were calculated, the matrix

diagonalized, and the parameters, g_J , A, and B adjusted to obtain the best fit of the energies of the transitions to the microwave frequency. There was no way of adjusting the wavefunctions of the Γ_8 state except by starting the calculations over with a new set calculated for a different x value. In a separate program we took the parameters obtained in the fitting program and, by a iterative numerical process, obtained the magnetic field values that a set of parameters gave for a particular transition at a particular microwave frequency. These programs are checked by reproducing the data of Berlorizky, et al. for the $\text{Er}^{3+}:\text{MgO}$ ($I = 7/2$) system.

Results and Discussion

Initially, a few sets of data were chosen for various magnetic field orientations and these data were fit with various sets of Γ_8 wavefunctions corresponding to different x values. For $x < 0$ the best fit was obtained for $x = -.575$. The data was much less sensitive to the positive values of x; almost the same quality fit could be obtained for $.45 < x < .83$. This relative insensitivity to x at $x \sim .65$ is shown in Fig. 2 by the slowly varying values of P and Q in this region. It was found that the epr spectrum for a particular magnetic field orientation could be fitted quite satisfactorily. However, if all the data for a particular plane of rotation was fitted, the deviation between the calculated spectrum and the experimental points was quite marked. Figure 3 shows the variation of the fitted parameters g_J and A as a function of x for the high and low field.

transitions in the 111 and 110 planes, while Fig. 4 shows the calculated and measured transitions at $x = .50$ for the 110 and 111 planes for a particular set of parameters. For $x > .7$ the empirical parameters from a high-field fit caused a significant shift to lower field for the low field transitions calculated from the high field parameters. Similarly if the low field spectrum was fitted and the high field spectrum calculated, the center of gravity of the calculated high field spectrum was shifted to higher magnetic fields.

These results suggest the magnetic field or Zeeman interaction is causing the Γ_6 and $\Gamma_8^{(2)}$ states to be mixed. At high magnetic fields more of the Γ_6 state is admixed into the ground state and the parameters of Eq. (1) are adjusted empirically to reflect this mixing. Since the g value of the Γ_6 state ($3.667 g_J$) should be larger than for the high field $\Gamma_8^{(2)}$ state, this mixing will tend to make the actual $\Gamma_8^{(2)}$ spectrum appear at lower fields than it would if no mixing were present. The empirical parameters of Eq. (1) are adjusted by the least-squares program to reflect this mixing even though there is no allowance for it in the Hamiltonian. When these empirical parameters are used to calculate the low field spectrum (where the Zeeman mixing is much less) they give a calculated spectrum which is shifted to lower field because the high field parameters are overcompensated for the lower field. By a similar argument, the shift is to higher field in the high field spectrum if the fit is done with the low field data. This magnetic field mixing between the $\Gamma_8^{(2)}$ and the Γ_6 states

is anisotropic,⁴ will occur for all x values, and may be the reason that slightly different parameters are obtained for different magnetic field orientations. Because our present analysis does not take into account this Zeeman mixing we can only determine x as being in the range $.45 < x < .83$. This range is consistent with the data on Pa^{4+} and U^{4+} in CsZrCl_6 .

Some of the empirical parameters of Eq. (1) are shown in Table 2 for various x values and magnetic field orientations and planes of rotation. As shown in Fig. 3, the parameters g_J and A are fairly well determined but B is subject to a larger variation, and in some case a change of sign. The value of g_J is much reduced from the value $g_J = .769$ calculated from the parameters of Gruber and Menzel for the $J = 9/2$ ground state. However in an epr study of $\text{Np}(\text{BH}_4)_4$ diluted in $\text{Zr}(\text{BH}_4)_4$ for which the Γ_6 state is lowest, a value of $g_J = .515$ was obtained.⁹ The ratio $\frac{g_J}{A}$ agrees within $\sim 5\%$ for the two systems. This agreement suggests that the assumption of a pure J multiplet with no crystal field mixing is reasonable. Furthermore a complete calculation of the eigenvector for the ground crystal field state with the electrostatic, spin-orbit, and crystal field parameters for Cs_2NpCl_6 , and then with the crystal field parameters (free ion parameters as before) of U^{4+} in Cs_2ZrCl_6 shows that higher J states contribute less than 5% in the former system and less than 3% in the latter system. The reduction in g_J value seems much too large for a covalency effect and may be due to some dynamic effect such as spin-phonon interactions or Jahn-Teller coupling.¹⁰

Further work is underway on the optical spectrum of Np^{4+} in Cs_2ZrCl_6 and on a more complete analysis of the epr spectrum including the $\Gamma_6-\Gamma_8^{(2)}$ interactions.

ACKNOWLEDGEMENT

This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract No. W-7405-Eng-48.

Table 1. Values for the crystal field parameters of tetra-positive actinide ions in octahedral symmetry.

Crystal	$A_4 \langle r^4 \rangle$ (cm ⁻¹)	$A_6 \langle r^6 \rangle$ (cm ⁻¹)	x
Pa ⁴⁺ in Cs ₂ ZrCl ₆ ^a	888	41.9	.794
U ⁴⁺ in Cs ₂ ZrCl ₆ ^b	823	35.4	.810
Np ⁴⁺ in Cs ₂ NpCl ₆ ^c	520	150	.387

- a) J. D. Axe, Ph.D. Thesis, University of California, Berkeley, 1960, UCRL-9293; J. D. Axe, H. J. Stapleton, and C. D. Jeffries, Phys. Rev. 121, 1630 (1961).
- b) R. A. Satten, C. L. Schreiber, and E. Y. Wong, J. Chem. Phys. 42, 162 (1965).
- c) E. R. Menzel and J. B. Gruber, J. Chem. Phys. 54, 3857 (1971).

Table 2. Typical Values of the Parameters of Equation (1).

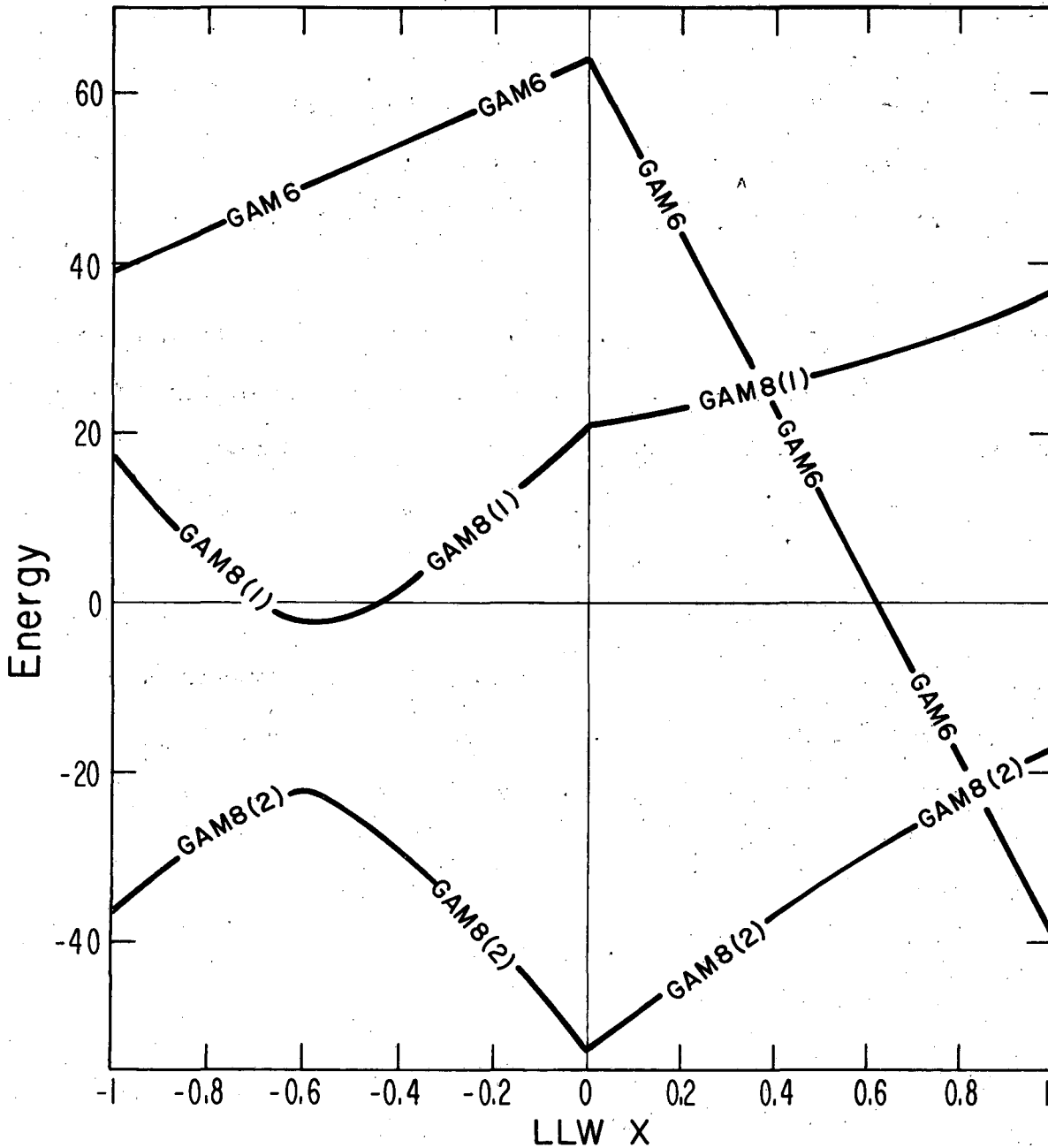
x	Plane of Rotation	Transitions	Frequency (GHz)	g_J	A (cm^{-1})	B (cm^{-1})
.50	110	High Field	35.28	.5623	.03332	$.271 \times 10^{-3}$
.50	110	Low Field	35.24	.5553	.03357	$.337 \times 10^{-3}$
.50	111	High Field	35.41	.5495	.03440	$-.222 \times 10^{-3}$
.50	111	Low Field	35.39	.5535	.03506	$.123 \times 10^{-3}$
.76	110	High Field	35.28	.6303	.03721	$.201 \times 10^{-3}$
.76	110	Low Field	35.24	.5530	.03338	$.358 \times 10^{-3}$
.76	111	High Field	35.41	.6200	.04002	$-.179 \times 10^{-3}$
.76	111	Low Field	35.39	.5482	.03485	$.131 \times 10^{-3}$

REFERENCES

1. J. E. Bray, Phys. Rev. B18, 2973 (1978).
2. K. R. Lea, M.J.M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).
3. The formulation of this problem is described in Reference 4.
4. A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford, 1970.
5. Y. Ayant, E. Belorizky, and J. Rosset, J. Physique 23, 201 (1962).
6. E. R. Menzel and J. B. Gruber, J. Chem. Phys. 54, 3857 (1971).
7. E. Belorizky, Y. Ayant, D. Descampes, and Y. M. d'Aubigné, J. Physique 27, 313 (1966).
8. N. F. Ramsey, "Molecular Beams", Oxford University Press, London, 1963.
9. R. Banks and N. Edelstein, private communication.
10. B. R. Judd, in "Proceedings of the 2nd International Conference on the Electronic Structure of the Actinides", J. Mulak, W. Suski, and R. Troc, editors, Polish Academy of Sciences, Wroclaw, 1977.

FIGURE CAPTIONS

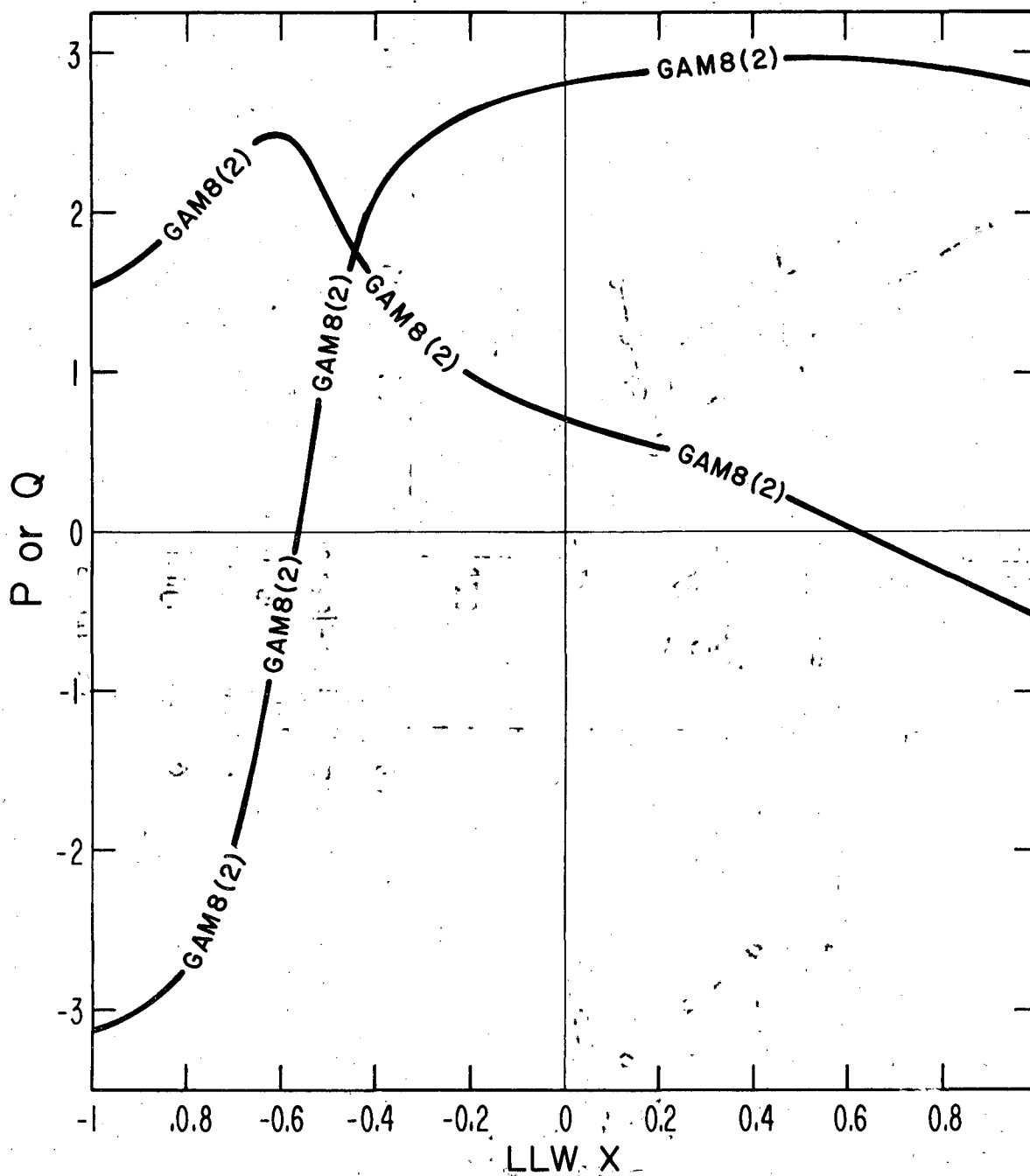
- Figure 1. Energy level diagram for a $J = 9/2$ state in octahedral symmetry as a function of x .
- Figure 2. Values of P or Q for the $\Gamma_8^{(2)}$ state as a function of x .
- Figure 3. Values of g_J (left hand side) and A (right hand side) as a function of x derived from a least-square fit.
- Figure 4. Fit of the experimental and calculated spectra in the 111 and 110 planes for $x = .50$; $g_J = .556$, $A = .0339 \text{ cm}^{-1}$, and $B = .0002 \text{ cm}^{-1}$. The angles shown in the graph for the 111 plane low field experimental data should be multiplied by -1 . The crystalline axes from which the angles are measured are the [110] and the [001] for the 111 plane and the 110 plane, respectively.



Lea, Leask, Wolf diagram $J = 9/2$

XBL 793-9048

Figure 1



Lea, Leask, Wolf diagram $J = 9/2$

XBL 793-9049

Figure 2,

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