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E. Gamp and N. Edelstein

September 1983

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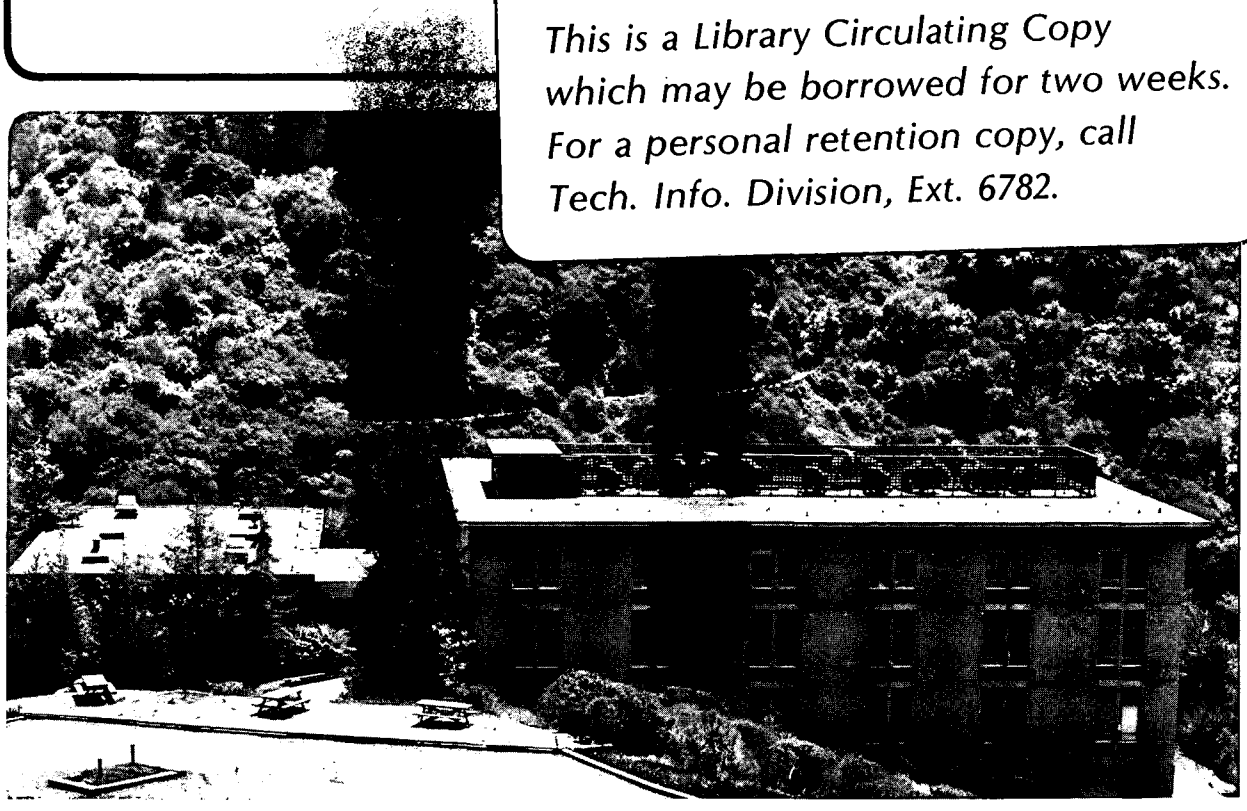

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Effects of Small Distortions on the EPR of the Γ_6 State (T_d Symmetry) of $Np(BH_3CH_3)_4$ Diluted in $Zr(BH_3CH_3)_4$[a]

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Abstract

The single crystal and powder EPR spectra of $^{237}Np(BH_3CH_3)_4$ diluted in $Zr(BH_3CH_3)_4$ are reported and interpreted in terms of an orthorhombic spin Hamiltonian with $g_x = 1.7739(4)$, $g_y = 1.8292(4)$, $g_z = 1.7961(5)$, $A_x = 0.1079(2)\ cm^{-1}$, $A_y = 0.1153(2)\ cm^{-1}$, $A_z = 0.1135(2)\ cm^{-1}$. A modified point charge calculation indicates qualitatively that very small deviations of the site symmetry from T_d are enough to account for the observed splitting of the g values.

Introduction

We have recently reported the syntheses and structures of the volatile isostructural compounds $Np(BH_3CH_3)_4$ and $Zr(BH_3CH_3)_4$.[1]

At room temperature the unit cell is tetragonal containing two equivalent molecules related by symmetry. The metal atom is tetrahedrally coordinated to the four methylhydroborate groups by three hydrogen bridge bonds per group summing to a nearest-neighbor coordination number of 12. The local symmetry about the metal atom is similar to that found for $Np(BH_4)_4$, $Zr(BH_4)_4$, and $Hf(BH_4)_4$[2-4] except for the replacement of the terminal hydrogens by methyl groups.

The open shell electron configuration for the Np^{4+} ion is $5f^3$ with the lowest level characterized by J = 9/2. In a site of T_d symmetry as found in crystals of $Np(BH_4)_4$ diluted in $Zr(BH_4)_4$, the ground crystal field state has Γ_6 symmetry and is isotropic in a magnetic field.[5,6] The same behavior was expected for $Np(BH_3CH_3)_4$ diluted in $Zr(BH_3CH_3)_4$. However, it has been found that $Np(BH_3CH_4)_4/Zr(BH_3CH_4)_4$ exhibits anisotropic behavior in a magnetic field and has an average g value considerably different than its tetrahydroborate analog. This latter effect has been discussed in an earlier paper.[7] In this work we present the EPR measurements for $Np(BH_3CH_3)_4/Zr(BH_3CH_3)_4$ and propose a model to qualitatively explain the results.

Experimental

The syntheses of $Np(BH_3CH_3)_4$ amd $Zr(BH_3CH_3)_4$ have been described previously.[1] Single crystals of $Zr(BH_3CH_3)_4$ doped with $^{237}Np(BH_3CH_3)_4$ were grown by first adding approximately 1 mg of $Np(BH_3CH_3)_4$ to 50 mg $Zr(BH_3CH_3)_4$ in a long pyrex tube in an inert atmosphere box. The tube was then evacuated to 10^{-4} Torr and sealed off. Single

crystals were obtained by slow cosublimation in the top of the tube upon heating the lower half to approximately 30°C. These crystals were sealed into 2 mm ID quartz tubes and oriented for EPR measurements by x-ray identification of the faces and edges. They were also checked for twinning by x-ray methods. Powder samples were obtained by grinding the crystals and sealing them into 2 mm OD quartz tubes. Solution samples were prepared by dissolving ~ 1 mg of freshly sublimed $^{237}Np(BH_3CH_3)_4$ in approximately 2 ml of very dry, degassed methylcyclohexane. The highly unstable solution was then sealed into a 3 mm OD quartz tube, and the spectrum obtained at ~ 2 K within an hour. EPR spectra at 35 GHz were obtained using a VARIAN E110 microwave bridge and a electromagnet which could be rotated about the vertical axis. The maximum field that could be obtained was 16 kGauss. The magnetic field was monitored with an NMR gaussmeter and the microwave frequency with a frequency counter.

Results

The single crystal spectrum of $Np(BH_3CH_3)_4/Zr(BH_3CH_4)$ clearly indicates the presence of two inequivalent sites in the $Zr(BH_3CH_3)_4$ at 2 K (see Figure 1). In addition a considerable anisotropy of the resonance fields was observed when the angle of the magnetic field with respect to the crystal axes was varied (Figure 2a,2b).

These results can be summarized in terms of the parameters of a spin Hamiltonian[8]

$$H = \beta(g_xH_xS_x'+g_yH_yS_y'+g_zH_zS_z') + A_xS_x'I_x + A_yS_y'I_y + A_zS_z'I_z \qquad (1)$$

where the effective spin $S' = 1/2$, the nuclear spin of ^{237}Np $I = 5/2$; β is the Bohr magneton; g_k, A_k, $k = x,y,z$ are the principal axes of the g and A tensor which are assumed to be parallel; and H_k are the components of the magnetic field with respect to these tensor axes. We were not able to observe the highest field hyperfine line of the spectrum because the resonance lies outside the limits of the electromagnet used.

The orientation and magnitude of the g and A tensor were determined by performing least squares fits to the spectra and their angular dependence using the Breit-Rabi formula.[9] The values of the g and A tensors were found to be the same for both observed sites within experimental error and are listed in Table 1. However their orientation in the two sites differs by a rotation of 90° around the crystallographic c axis of the $Zr(BH_3CH_3)_4$ host. The room temperature crystal structure of $Zr(BH_3CH_3)_4$ is tetragonal (space group $P4_2/n$) with two molecules per unit cell.[1] From the angular dependence of the EPR spectrum, it was determined that $g_z(A_z)$ for both sites is parallel to the c axis and the $g_x(A_x)$ and $g_y(A_y)$ axes are parallel to the projections of the Zr–B bonds on the a–a plane. This is shown in Figure 3. The g and A tensor of each site were found to be parallel within experimental error (± 2°). Resonance fields calculated from the above orientations and the parameters in Table 1 are indicated as solid lines in Figure 2.

To confirm the above analysis a powder spectrum of the ground crystals was recorded. It is shown in Figure 4b and exhibits the

expected features of a slightly orthorhombically distorted system with $S' = 1/2$ and $I = 5/2$. Again, the highest field resonance could not be recorded due to the limits of the electromagnet.

The principal g and A values determined from the powder agreed within experimental error with those found in the least squares fits of the single crystal rotations. To get more information about the influence of the surrounding lattice on the spectrum of the $Np(BH_3CH_3)_4$ moiety, the spectrum of a glassy solution of the compound in methylcyclohexane was recorded and is shown in Figure 4a. No anisotropy within experimental error (~ 10 Gauss) of the resonances was found. The isotropic g and A values obtained from a least squares fit of the five observed resonances are also listed in Table 1.

Discussion

The EPR spectrum of the $\Gamma_6(f^3)$ state in T_d symmetry should be isotropic.[8] The analysis of the optical spectrum and the susceptibility[7] have confirmed that no magnetically anisotropic Γ_8 state is low enough to be thermally populated at 2 K or to mix with the Γ_6 states via the Zeeman effect. Furthermore, any electronic reason for the observed anisotropy can also be ruled out from the observation of an isotropic spectrum from the frozen glassy solution of $Np(BH_3CH_3)_4$ in methylcyclohexane with approximately the same A and g values as the average of those found in $Np(BH_3CH_3)_4/Zr(BH_3CH_3)_4$. A possible explanation for these experimental results is that the host crystal undergoes a phase transition on cooling from room temperature to 2 K or upon the inclusion of the impurity $Np(BH_3CH_3)_4$. This

change in structure would have to be small as the single crystals used in the EPR experiments did not crack or become opaque even after repeated cycling from room temperature to 2 K.

In order to obtain an idea of the sensitivity of the g value to the geometry of the crystal field in $Np(BH_3CH_3)_4$, we performed the following calculation. The crystal field parameters B_q^k were related to ligand positions using the point charge model[10,11] in the following way. If we assume the n ligands to be point charges $-g_j\varepsilon$ with spherical coordinates $(\rho_j, \alpha_j, \beta_j)$, the B_q^k can be expressed in terms of these coordinates:

$$B_q^k = (-1)^q \left[\frac{(k-q)!}{(k+q)!}\right]^{1/2} \langle r^k \rangle \sum_{j=1}^{n} \frac{g_i \varepsilon^2}{\rho_j^{k+1}} P_k^q (\cos \alpha_j) e^{-iq\beta_j} \quad (2)$$

Here P_k^q (cos α) are associated Legendre polynomials, ε is the electron charge and $\langle r^k \rangle$ is the expectation value of r^k which is obtained from ab initio calculations. The $\langle r^k \rangle$ used in this work are average relativistic Dirac-Slater values calculated for Np^{4+} by Lewis and coworkers.[12] In T_d symmetry the only independent B_q^k are B_0^4 and B_0^6 (see previous paper). In a NpH_{12} cluster (twelve hydrogen ligands lying on the centers of the edges of a cube) they are both calculated to be negative which is in agreement with the optical analysis. A NpB_4 unit (four borons at the corners of a tetrahedron) leads to a positive B_0^4 and negative B_0^6 and will not be considered further.

The point charge g_jE and the distance ρ_i from the central ion were now treated as free parameters to describe the crystal field and varied in equation 2 until the experimental values of B_0^4 and B_0^6 were obtained.

These parameters were found to be $g_j = -0.0497$ esu per hydrogen and $\rho_j = 1.167$Å. It should be emphasized that these values do not have any physical meaning (the experimental Np–H distance is 2.16Å[1]) but serve only to parameterize the T_d crystal field.

In the next step, a distortion was introduced to lower the symmetry of the NpH_{12} unit from T_d to orthorhombic. A simple way to accomplish this is by changing the spherical coordinate β_j of each hydrogen by an amount δ while keeping ρ_j and α_j fixed. The distortion is illustrated in Figure 5. To symbolize the rigidity of each BH_3–CH_3 unit, they are represented as triangles. For a positive δ, triangles 1 and 2 rotate clockwise around z and triangle 3 and 4 counterclockwise. This movement lowers the symmetry of the NpH_{12} unit from T_d to D_2. The crystal field Hamiltonian now has to be extended to orthorhombic symmetry and becomes

$$E_{CF} = \sum_{k=2,4,6} [B_0^k C_0^{(k)} + \sum_{q=2}^{k} B_q^k (C_{-q}^{(k)} + C_{+q}^{(k)})]; \text{ q even} \qquad (3)$$

Using equation 2 and g_j and ρ_i as determined above in cubic symmetry, the necessary B_q^k were calculated as a function of the distortion δ. This variation is shown in Table 2. Using these

B_q^k and the free-ion parameters found in the optical analysis[7] of $Np(BD_4)_4/Zr(BD_4)_4$, g_x, g_y and g_z of the ground state were calculated in the complete f^3 basis. An orbital reduction factor $k = 0.862$ was included to reduce the average g value to the experimental value of 1.800 found in $Np(BH_3CH_3)_4/Zr(BH_3CH_3)_4$. B_2^4, B_2^6 and B_6^6 were set to zero to reduce the computational effort.

The results are shown in Figure 6. They indicate that a single angular distortion of less than 1.5° is enough to account for the anisotropy found in the g-tensor of $Np(BH_3CH_3)_4/Zr(BH_3CH_3)_4$. A change of sign in the distortion parameter δ is equivalent to an exchange of the x and y axes while g_z should be unaffected and remain constant as is easily seen from Figure 5. The small deviations from this behavior seen in Figure 6 are due to the neglect of B_2^4, B_2^6 and B_6^6 in the calculation. Of course, other distortions than the one above or packing effects due to the different size of the Np^{4+} and Zr^{4+} ion could also cause the anisotropy of the EPR spectrum. In spite of the rather crude model used for the calculation, it shows clearly the extreme sensitivity of the EPR spectrum of the $\Gamma_6(5f^3)$ state to structural changes.

Conclusions

The anisotropic EPR spectrum of ^{237}Np-methylborohydride diluted in Zr-methylborohydride can be explained as the result of a small orthorhombic distortion of the host lattice.

This paper qualitatively shows the extreme sensitivity of the EPR

spectrum of ^{237}Np-borohydrides to changes in the crystal field. Very small distortions can be detected and the replacement of BH_4^- ligands by BH_3-CH_3^- induces remarkable changes. The data indicate the considerable influence of the ligands on the $5f^3$-shell in Np^{4+}.

Table 1

Spin Hamiltonian Parameters for $^{237}Np((BH_3CH_3)_4$

Host	$Zr(BH_3CH_3)_4$	$CH_3C_6H_{11}$ [a]	$Zr(BH_4)_4$ [b]
g_x	1.7739(4)	1.8126(4)	1.894(2)
g_y	1.8292(4)		
g_z	1.7961(5)		
$A_x(cm^{-1})$	0.1079(2)	0.1124(1)	0.1140(10)
$A_y(cm^{-1})$	0.1153(2)		
$A_z(cm^{-1})$	0.1135(2)		
g_{ave} [c]	1.7997(4)	1.8126(4)	1.894(2)
$A_{ave}(cm^{-1})$	0.1122(2)	0.1124(1)	0.1140(10)

[a] frozen solution (glass).
[b] $^{237}Np(BH_4)_4$ in $Zr(BH_4)_4$, reference 7.
[c] averaged ("isotropic") values.

Table 2. Dependence of the crystal field parameters (cm^{-1}) on the distortion parameter δ (NpH_{12} unit, point charges of -0.0497 esu per hydrogen)

$\delta(°)$	B_0^2	B_2^2	B_0^4	B_2^4	B_4^4	B_0^6	B_2^6	B_4^6	B_6^6
-2.5	0.	-430.	-2722.	214.	-1602.	-5070.	-232.	9341.	1023.
-2.0	0.	-344.	-2722.	172.	-1611.	-5070.	-186.	9393.	822.
-1.5	0.	-258.	-2722.	129.	-1618.	-5070.	-139.	9433.	618.
-1.0	0.	-172.	-2722.	86.	-1623.	-5070.	-93.	9462.	413.
-0.5	0.	-86.	-2722.	43.	-1626.	-5070.	-46.	9479.	207.
0	0.	0.	-2722.	0.	-1627	-5070.	0.	9485.	0.
0.5	0.	86.	-2722.	-43.	-1626.	-5070.	46.	9479.	-207.
1.0	0.	172.	-2722.	-86.	-1623.	-5070.	93.	9462.	-413.
1.5	0.	258.	-2722.	-129.	-1618.	-5070.	139.	9433.	-618.
2.0	0.	344.	-2722.	-172.	-1611.	-5070.	186.	9393.	-822.
2.5	0.	430.	-2722.	-214.	-1602.	-5070.	232.	9341.	-1023.

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Figure 1. Single crystal EPR spectrum of $Np(BH_3CH_3)_4/Zr(BH_3CH_3)_4$ at 2 K. Microwave frequency is 34.700 GHz, orientation of the magnetic field perpendicular to the c-axis.

Figure 2. Angular dependence of resonance fields: a) rotation in the a-a plane, ϕ is the angle of the magnetic field with the crystallographic ⟨110⟩ plane; b) rotation in the ⟨110⟩ plane, θ is the angle of the magnetic field with the c-axis, solid lines were calculated from the parameters in Table 1.

Figure 3. Orientation of the g-tensor axes in the crystallographic unit cell. The view is along the c-axis, the Zr(Np) atoms are located at (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75). Hydrogen positions are not indicated.

Figure 4. a. Spectrum of a ~ 1.5×10^{-3} M glassy solution of $^{237}Np(BH_3CH_3)_4$ in methylcyclohexane at 2 K; microwave frequency: 34.848 GHz.

b. Powder spectrum at 2 K, microwave frequency: 34.700 GHz.

Figure 5. Orthorhombic distortion of the NpH_{12} cluster which lowers the symmetry from T_d to D_2. The rigidity of each H_3B–R ligand is indicated by triangles which connect the coordinating H atoms of each ligand. Arrows indicate distortion for δ positive.

Figure 6. Influence of the orthorhombic distortion δ on the g values and the energy in the lowest Γ_8 state. Arrows indicate the experimental g values.

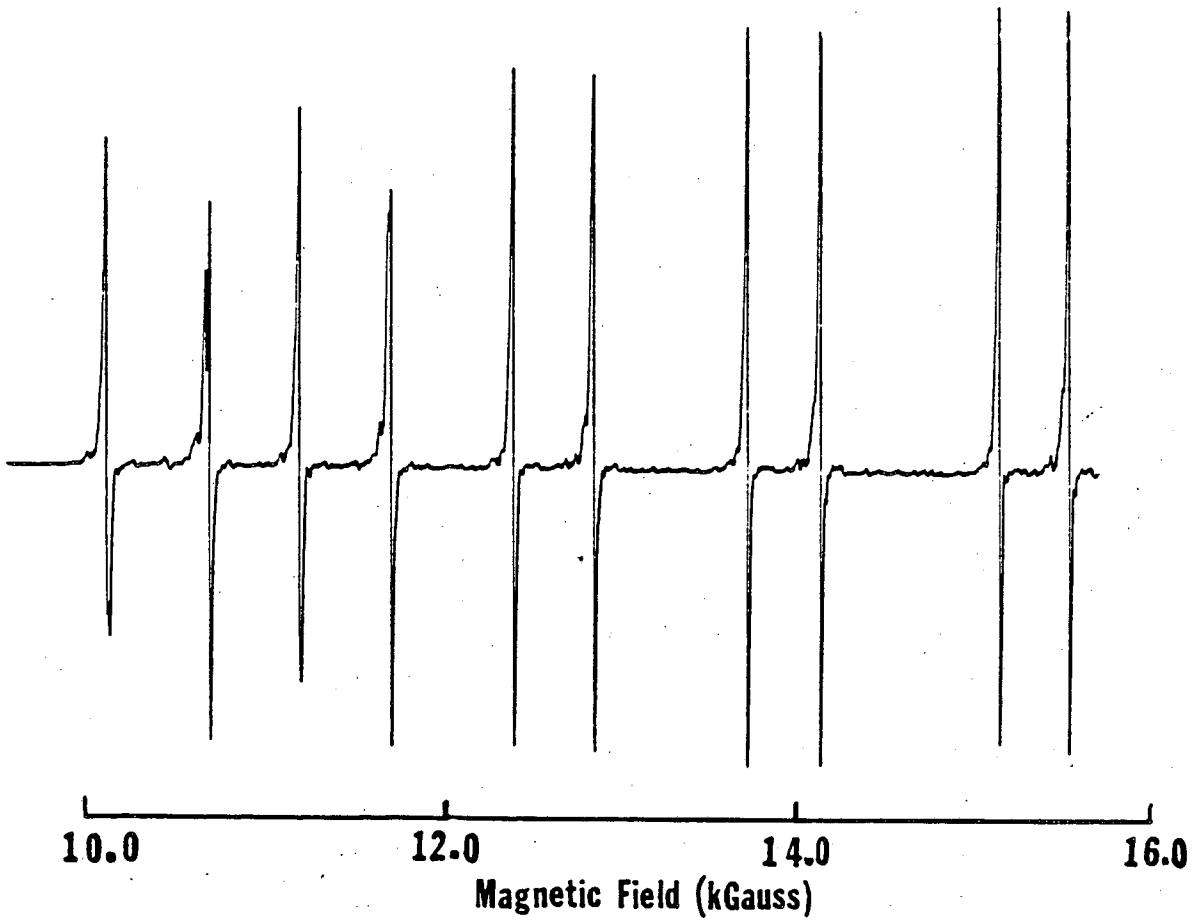

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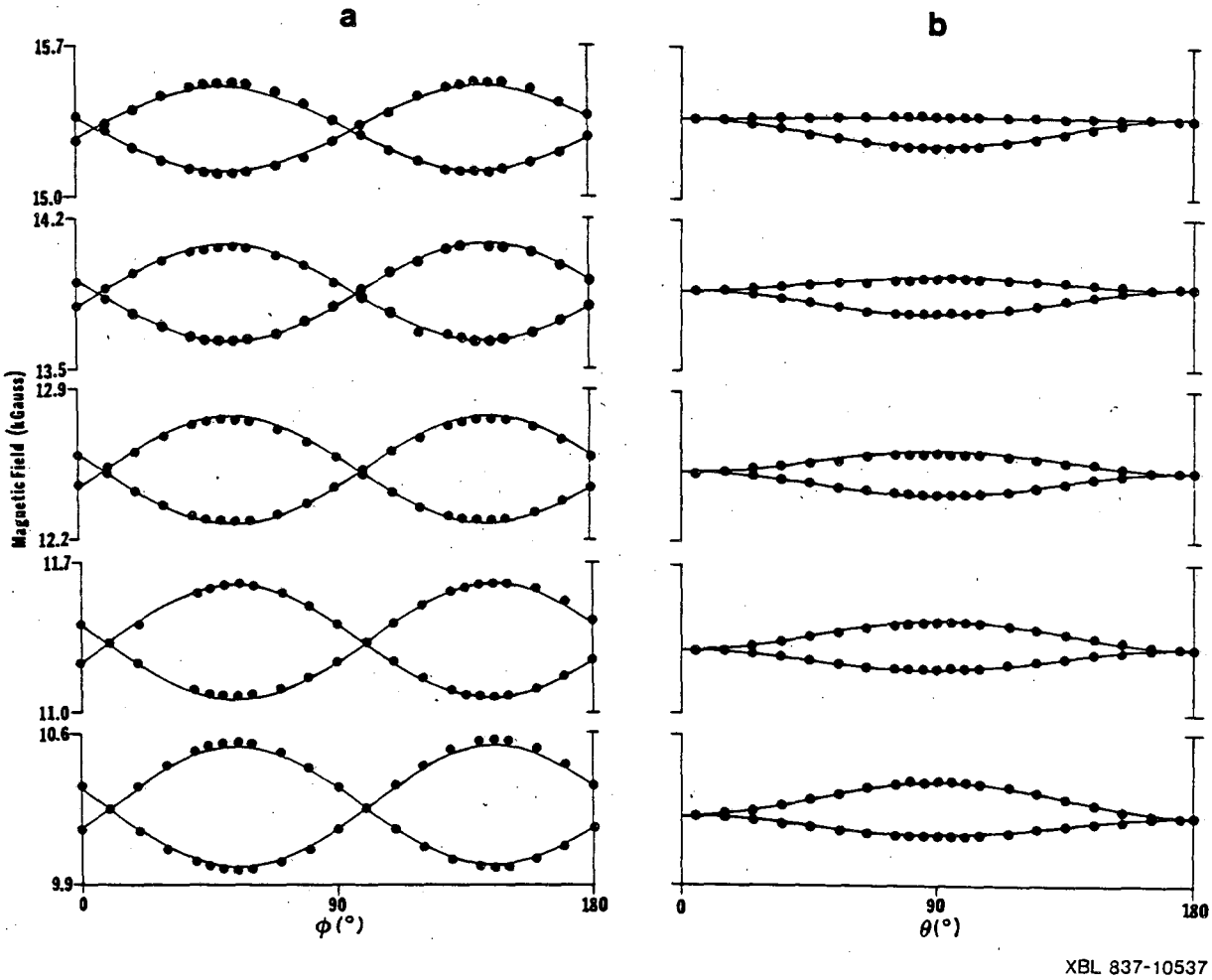
Figure 1


a
b
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15.0
14.2
13.5
12.9
12.2
11.7
11.0
10.6
9.9
Magnetic Field (kGauss)
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0
90
180
θ(°)
XBL 837-10537

Figure 2

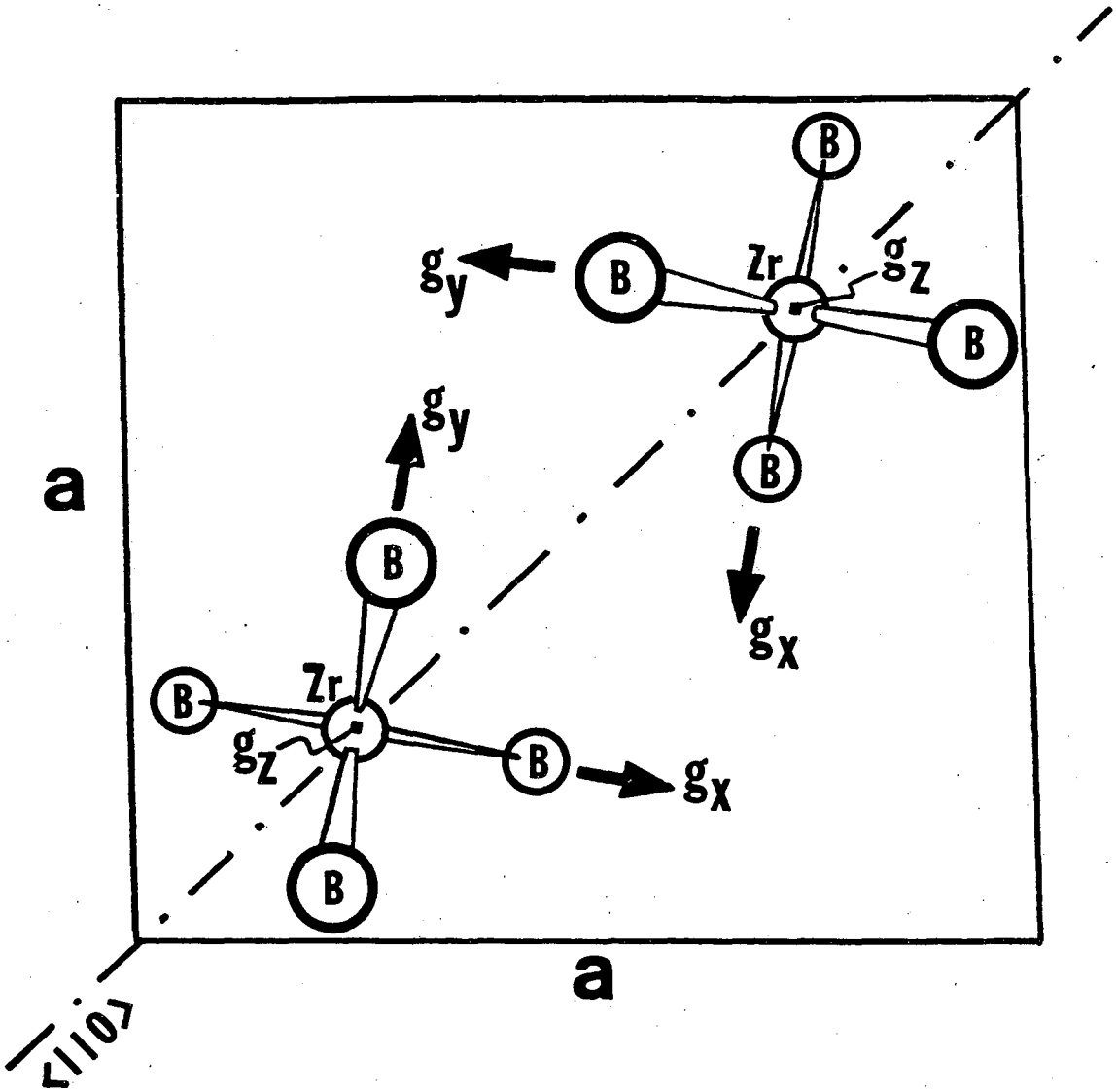

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Figure 3

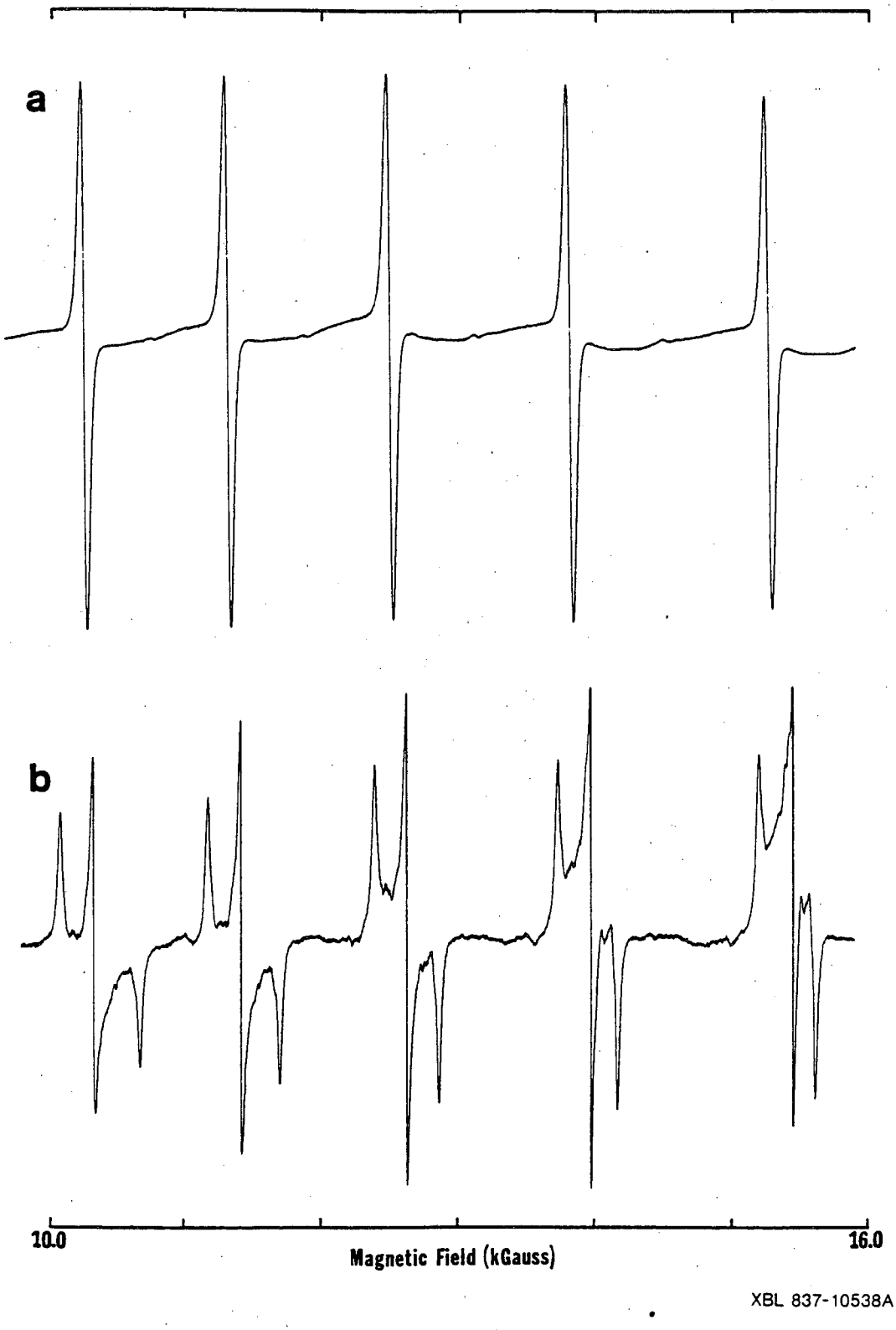

Figure 4

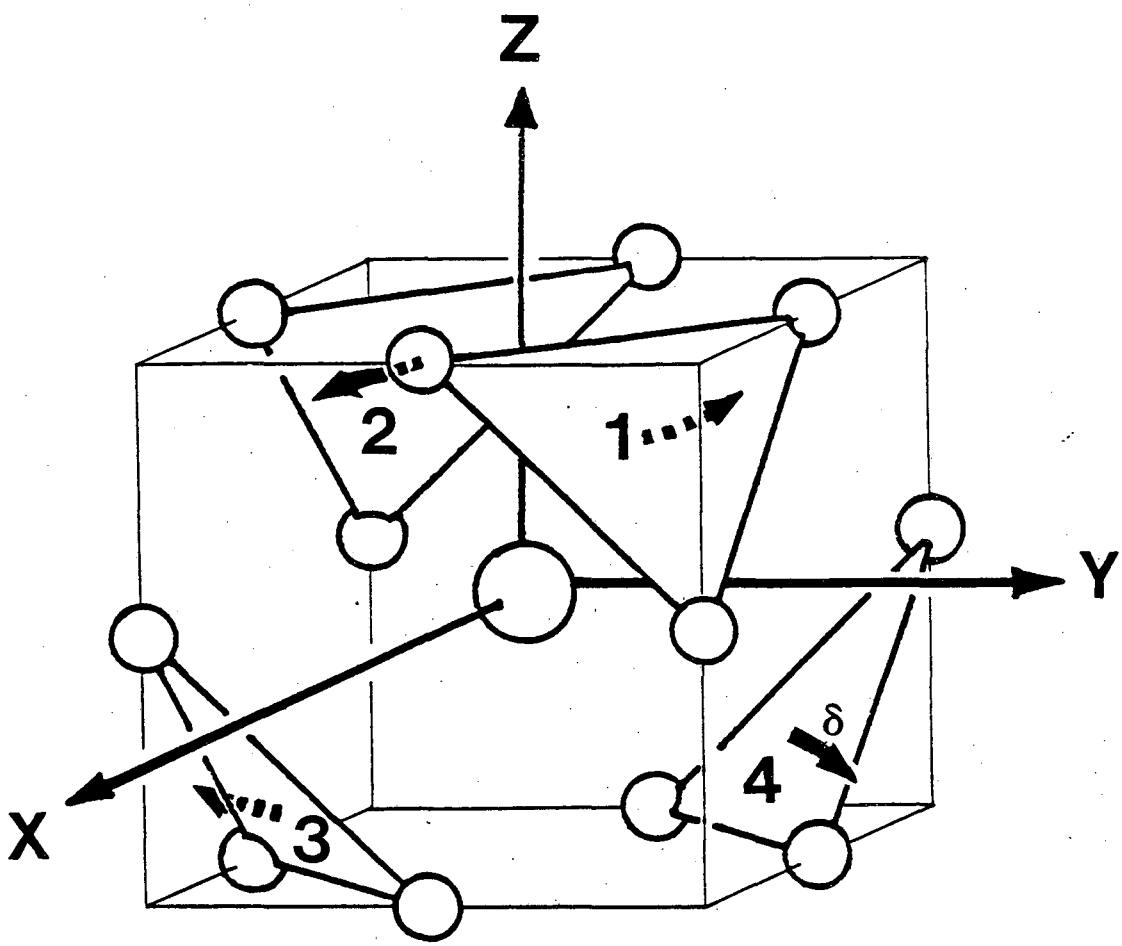

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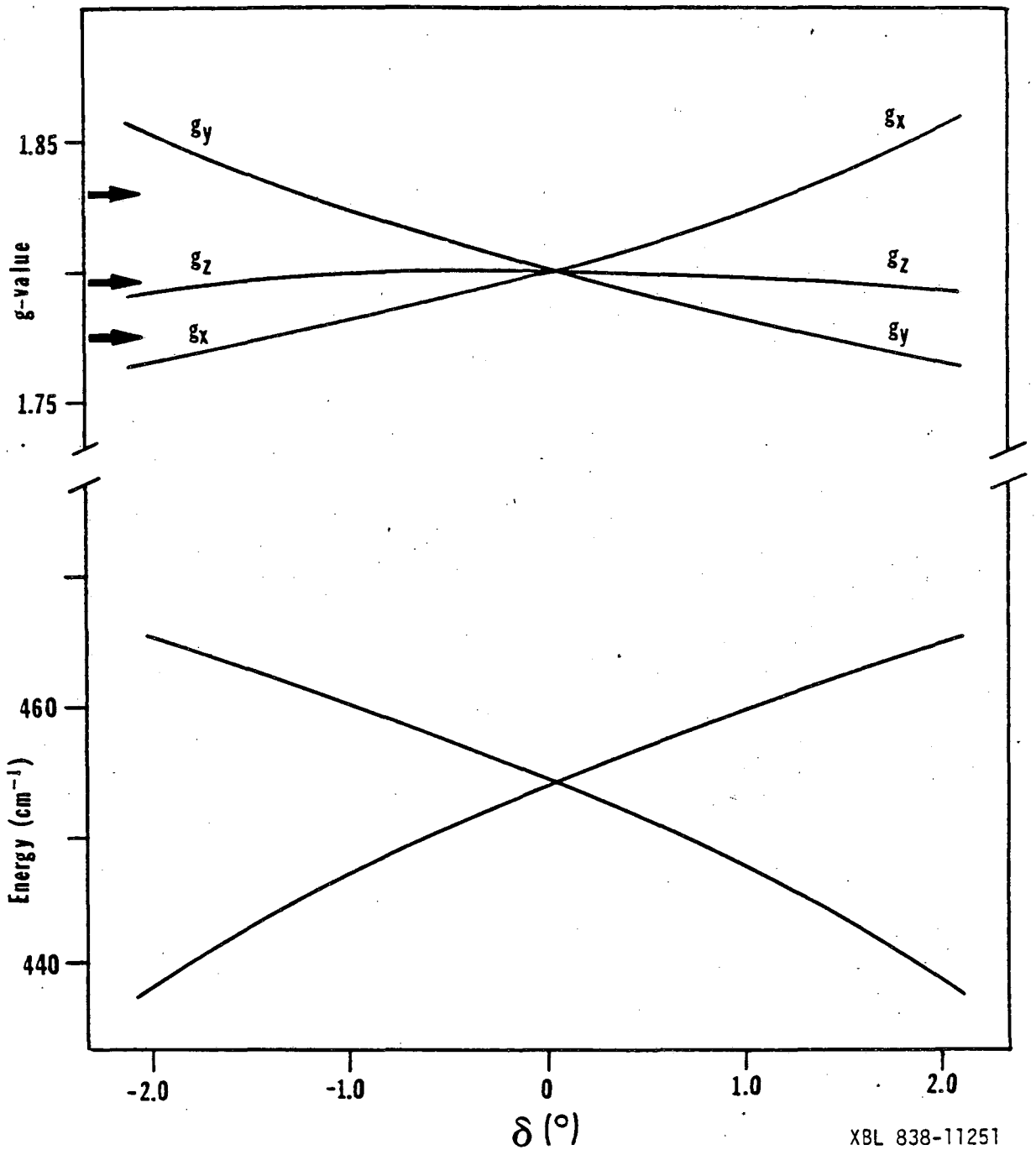
Figure 5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δ (°)
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Figure 6

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