Influence of localized anharmonic vibrations on electron paramagnetic resonance spectroscopy

N. V. Vugman and M. Rothier Amaral, Jr.

Instituto de Física, Universidade Federal do Rio de Janeiro, Ilha do Fundão,
Rio de Janeiro 21945, Brazil

We have developed a theory that provides an interpretation for the temperature dependence of the g values measured by electron paramagnetic resonance (EPR) spectroscopy, based on the presence of localized low-frequency anharmonic modes. The model is successfully applied to EPR data on paramagnetic nickel cyanide complexes in NaCl host lattice, for both d_{z^2} and $d_{x^2-y^2}$ ground states.

I. INTRODUCTION

The temperature influence on electron paramagnetic resonance (EPR) spectra has been frequently interpreted with the aid of the dynamic Jahn-Teller effect.[1] In a classical paper,[2] O'Brien discusses the nature of the electronic-vibrational states of a d^9 ion in an octahedral complex considering an adiabatic model, and derived expressions for the g values and the hyperfine structure parameters of the EPR spectrum at high and low temperatures. Vibronic mixing between the d_{z^2} and $d_{x^2-y^2}$ orbitals lead to an anisotropic EPR spectrum at low temperatures, which changes at some intermediate temperature to a high-temperature isotropic spectrum. This model was successfully applied to the work of Bleaney *et al.*[3] on the Cu^{2+} ion in $Mg_3La_2(NO_3)_{12} \cdot 24D_2O$ host lattice.

EPR studies of transition-metal cyanide complexes diluted in alkali-metal halide host lattices and submitted to ionizing radiation revealed that hexacoordinated complexes of Fe, Ru, Os, Co, Rh, and Ir are reduced by capture of an electron in a d_{z^2} antibonding molecular orbital.[4] This investigation also showed that square-planar complexes of Ni and Pd (Refs. 5 and 6) exhibit both oxidized and reduced states. For example, electron-irradiated diamagnetic Ni(II) d^8 cyanide complexes in a potassium chloride host lattice give rise to paramagnetic d^7 $[Ni(CN)_4Cl_2]^{3-}$ complexes (unpaired electron in a d_{z^2} orbital) and to paramagnetic d^9 $[Ni(CN)_4Cl_2]^{5-}$ complexes (unpaired electron in a $d_{x^2-y^2}$ orbital). The simultaneous observation of a transition-metal ion in two different charge states, imbedded in the same host lattice, makes these systems particularly suitable for comparative measurements of properties which depend on external factors.

Careful EPR measurements show that the spin Hamiltonian parameters for these paramagnetic complexes are temperature dependent. For paramagnetic species with the unpaired electron in a d_{z^2} orbital, the parallel component of the g tensor is temperature independent within the experimental accuracy. The perpendicular g factor, however, continuously increases with the temperature.

On the other hand, for paramagnetic species with the unpaired electron occupying a $d_{x^2-y^2}$ orbital, both parallel and perpendicular g values continuously increase with temperature. It is clear that these results cannot be interpreted on the basis of the dynamic Jahn-Teller effect.

In the present investigation we propose an explanation for the observed temperature dependence of the g values measured for d^7 and d^9 complexes. These temperature effects are interpreted in terms of localized anharmonic vibrations. Using this framework we shall compute thermal atomic displacements and use crystal-field theory to calculate the temperature dependence of the g values.

II. THEORY

A. The crystal-field model and localized anharmonic vibrations

In order to formulate a theory to interpret the g-tensor temperature dependence in cyanide complexes we shall begin with a crystal-field model. A ligand field picture would give a better description for such covalent complexes, but it would introduce too many parameters to deal with in a feasible way.[7]

Let us assume an hexacoordinated molecule, as shown in Fig. 1, with intramolecular distances a, b, c, and f (C_{2v} symmetry). The crystal-field eigenfunctions and energies are calculated and listed in the Appendix. The energies are written in units of $C(Ze\langle r^2 \rangle/7)$. The average value of r^n in the unpaired electron wave function is $\langle r^n \rangle$, and the constant C has been introduced in order to adjust the g values at $T=0$ K. The ratio $R = \langle r^4 \rangle / \langle r^2 \rangle$ may be calculated using the average values reported by Freeman and Watson.[8]

The main components of the g tensor are calculated from first-order perturbation theory.[1] For a d^7 system, d_{z^2} ground orbital with energy E_2, it follows that

$$g_{zz} = 2.0023 + 8\lambda \sin^2\gamma /(E_2 - E_{xy}) , \tag{1}$$

$$g_{xx} = 2.0023 + 2\lambda(\sqrt{3}\cos\gamma + \sin\gamma)^2 /(E_2 - E_{yz}) , \tag{2}$$

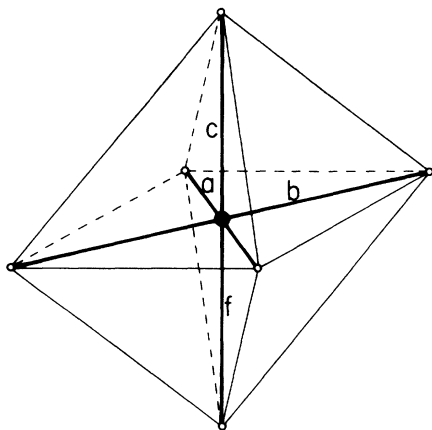$$g_{yy} = 2.0023 + 2\lambda(\sqrt{3}\cos\gamma - \sin\gamma)^2 /(E_2 - E_{xz}) . \tag{3}$$

FIG. 1. Intramolecular distances for an hexacoordinated complex.

For a d^9 system, $d_{x^2-y^2}$ ground orbital with energy E_1, we obtain

$$g_{zz} = 2.0023 + 8\lambda \cos^2\gamma / (E_1 - E_{xy}) \ , \tag{4}$$

$$g_{xx} = 2.0023 + 2\lambda(\cos\gamma - \sqrt{3}\sin\gamma)^2/(E_1 - E_{yz}) \ , \tag{5}$$

$$g_{yy} = 2.0023 + 2\lambda(\cos\gamma + \sqrt{3}\sin\gamma)^2/(E_1 - E_{xz}) \ , \tag{6}$$

where λ is the spin-orbit coupling constant for the transition metal in the appropriate charge state.

The energy differences between the two states mixed via spin-orbit coupling, which appear in the denominator of the expressions above, are written in terms of the intramolecular distances. We shall now assume that these energy differences are temperature dependent, which is possible if we consider that intramolecular distances are affected by the presence of localized anharmonic vibration modes, with frequencies low enough so that the corresponding vibrational energy levels can be populated at temperatures in which the experiments were performed. As vibration frequencies are 2 or 3 orders of magnitude larger than X-band Larmor frequencies, EPR spectroscopy "sees" the atoms at their average positions. Low-frequency vibration modes were predicted by Jones[9] from the vibrational spectra of Co, Rh, and Ir hexacyanides and were measured by Bloor in the far-infrared spectra of Fe and Co hexacyanides.[10]

In order to simplify the problem, we shall use the following assumptions: (1) The vibrations are independent. (2) The heavy central atom remains practically at rest. (3) The bending modes are constrained by the host lattice. (4) Each vibration mode is described by a Morse potential.

B. The generalized Morse potential

For a diatomic molecule, the Morse potential can be written as[11]

$$U(\rho) = D[1 - \exp(-h\rho)]^2 \ , \tag{7}$$

where $\rho = r - r_e$, D is the dissociation energy and h is a parameter that defines the length scale of the Morse po-

tential. The associated energies are,[11] in units of cm^{-1},

$$E(v) = \omega(v+\tfrac{1}{2}) - x\omega(v+\tfrac{1}{2})^2 \ , \tag{8}$$

where ω is the frequency in cm^{-1}, x is the anharmonicity parameter $\omega/(4D)$, and $v = 0, 1. \ldots$

Let us now consider the stretching modes of a polyatomic molecule with tetragonal symmetry. The normal coordinate for mode Γ can be written as [12]

$$Q_\Gamma = (n)^{-1/2} \sum_i \alpha_i^\Gamma \Delta d_i^\Gamma \ , \tag{9}$$

where the summation is to be performed over the n atoms involved in the vibration mode, $\alpha_i^\Gamma = \pm 1$ depending on the mode, and Δd_i^Γ is the displacement of atom i from its equilibrium position for mode Γ.

Let us assume that we can write expression (7) for each independent vibration, with the correspondence $Q_\Gamma \rightleftharpoons \rho$,

$$U(Q_\Gamma) = D_\Gamma[1 - \exp(-h_\Gamma Q_\Gamma)] \ , \tag{7a}$$

where D_Γ is the dissociation energy of the molecule if only mode Γ were excited. Some care must be taken with the definition of h_Γ. Comparison with the calculated frequencies for the stretching modes of a linear triatomic molecule[13] leads us to the relation

$$h_\Gamma = \omega_\Gamma \left[\frac{\mu}{2D_\Gamma} \right]^{1/2} . \tag{10}$$

For even modes, μ is equal to m, the mass of one ligand, and, for odd modes, μ equals $m/(1+2m/M)$, where M is the mass of the central atom.

C. Average values

Our aim is to evaluate average values for the coordinate Q_Γ for each energy level v of the Morse potential Q_Γ^v in order to calculate the thermal average of Q_Γ. Instead of dealing with cumbersome wave functions and integrals, we shall adopt a semiclassical point of view and write Q_Γ^v as the average of the turning points of the Morse potential for each energy level; that is,

$$Q_\Gamma^v = (Q_+^v + Q_-^v)/2 \ . \tag{11}$$

The turning points are calculated combining relations (7a) and (8) written for the mode in consideration. After some calculations we get

$$Q_\Gamma^v = -\frac{1}{2h_\Gamma} \ln(1 - E_\Gamma^v/D_\Gamma) \ . \tag{12}$$

The thermal average can be obtained from relation (12) and the Boltzmann distribution, taking into account that the Morse potential accommodates only a finite number of energy levels[11] given by

$$v_{max} = \frac{2D_\Gamma}{\omega_\Gamma} - 1 \ . \tag{13}$$

The thermal average is

$$Q_\Gamma(T) = -\frac{1}{2h_\Gamma} F_\Gamma(T) \ , \tag{14}$$

where

$$F_\Gamma(T) = \frac{\displaystyle\sum_0^{v_{max}} \ln(1 - E_\Gamma^v / D_\Gamma)\exp(-E_\Gamma^v / kT)}{\displaystyle\sum_0^{v_{max}} \exp(-E_\Gamma^v / kT)} \ . \tag{15}$$

On the other hand, the thermal average given by relation (9) can be written as

$$Q_\Gamma(T) = n^{-1/2} \sum_{i=1}^n \alpha_i^\Gamma \Delta d_i^\Gamma(T) \ . \tag{16}$$

Although there is a summation on the right-hand side of relation (16), considering that a vibration mode means a collective motion, we can comfortably assume that Δd_i^Γ and Q_Γ have the same temperature dependence. Therefore, it follows that

$$\Delta d_i^\Gamma(T) = -\frac{d_i(0)}{2h_\Gamma \alpha_\Gamma^i} F_\Gamma(T) \ , \tag{17}$$

which is the same for all atoms involved in a given mode, where $d_i(0)$ is the distance between the central metal and atom i at 0 K. Furthermore, if we consider a linear superposition of independent vibration modes, the net displacement of the i atom will be given by the sum of $\Delta d_i^\Gamma(T)$ over the vibration modes.

Finally, for a given temperature T, we get

$$d_i(T) = d_i(0) \left[1 - \frac{1}{2} \sum_\Gamma \frac{\alpha_i^\Gamma}{h_\Gamma} F_\Gamma(T) \right] \ . \tag{18}$$

This expression gives the intramolecular distances as a function of temperature. Substituting in relations (A1)–(A5), we may calculate the g values as a function of T. A least-squares method is used in order to fit the calculated g values to the experimental data. The parameters to be varied are frequency and dissociation energy for each mode to be considered, and the distances metal to the ligands at 0 K.

III. NICKEL CYANIDE COMPLEXES IN NaCl HOST LATTICE

Among the possible C_{4v} symmetry stretching modes, Fig. 2 shows only the ones considered for interpreting the temperature effects observed in the EPR spectra of monovalent and trivalent nickel cyanide complexes in NaCl host lattice with D_{4h} or approximate D_{4h} symmetry.[14] Mode A_{2u} is infrared active while modes A_{1g} and B_{1g} are Raman active. Figures 3 and 4 show their effect on the g values for a d_{z^2} and for a $d_{x^2-y^2}$ ground state, respectively, using the present theory. For the Ni^{3+} ion, $R = 2.057$ Å^2, and for the Ni^{1+} ion, $R = 3.7$ Å^2, obtained from extrapolation using the values for Ni^{4+}, Ni^{3+}, and Ni^{2+} taken from Ref. 8.

It is clear from Fig. 3 (top) that, if the unpaired electron occupies a d_{z^2} orbital, the axial modes A_{1g}^2 and A_{2u} play a very important role on the temperature dependence of the g factor considering an octahedral symmetry at 0 K. However, if we take a D_{4h} distortion at 0 K as
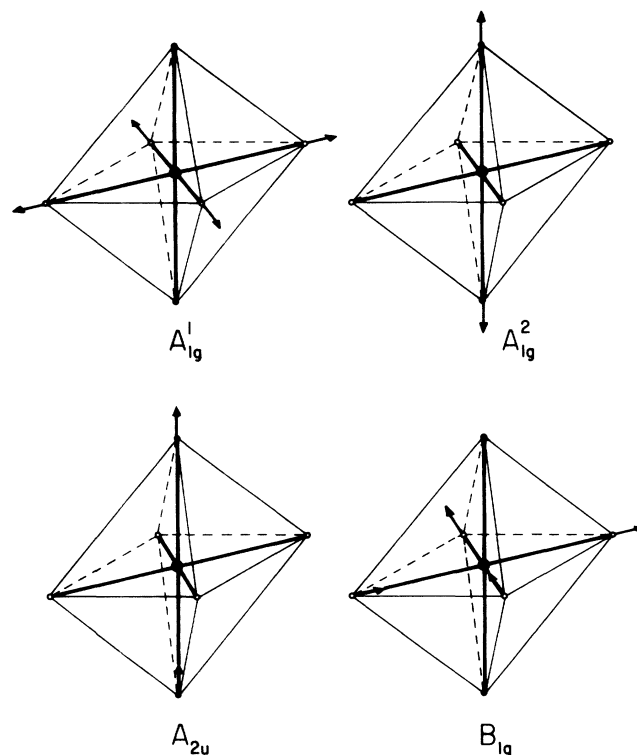

FIG. 2. Some stretching modes for C_{4v} symmetry.

shown in Fig. 3 (bottom), the contribution of the modes A_{1g}^1 and B_{1g} becomes more important for the same frequencies and dissociation energies. On the other hand, if the unpaired electron occupies a $d_{x^2-y^2}$ orbital, the equatorial modes A_{1g}^1 and B_{1g} are likely responsible for the major variations of the g values with temperature (see Fig. 4). Furthermore, it is known that the capture of an extra electron loosens its respective chemical bond,[4] which suggests that it may be possible to correlate the softening of the vibration modes to the presence of the unpaired electron in the corresponding molecular orbitals.

Table I displays the best fitting data for d^7 $[Ni(CN)_4Cl_2]^{3-}$ and for the d^9 $[Ni(CN)_4Cl_2]^{5-}$ paramagnetic complexes in NaCl host lattice. The respective fittings are shown in Figs. 5 and 6. The values of the metal to ligand distances, in and out of the equatorial plane, were frozen to 2 and 3 Å, respectively, which roughly correspond to the distance Ni-CN center of mass and to the NaCl lattice parameter.

The agreement between the experimental data and theory may be considered as very good, especially if we remember that the data for the $d_{x^2-y^2}$ ground state consist of two independent sets (g parallel and g perpendicular) which must be fitted with the same set of parameters. Notice that g values at 0 K have been adjusted by the introduction of the constant C.

The dissociation energies found are of the same order of magnitude as the energy necessary to thermally decompose a cyanide complex. Vibration frequencies also fall in the predicted range[10] and decrease when the
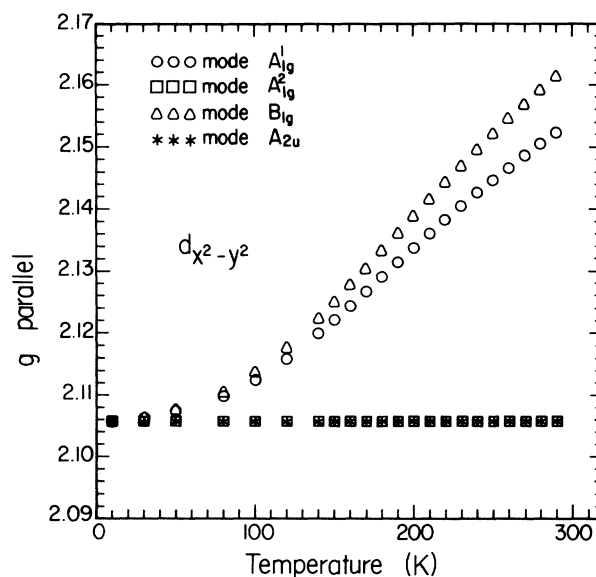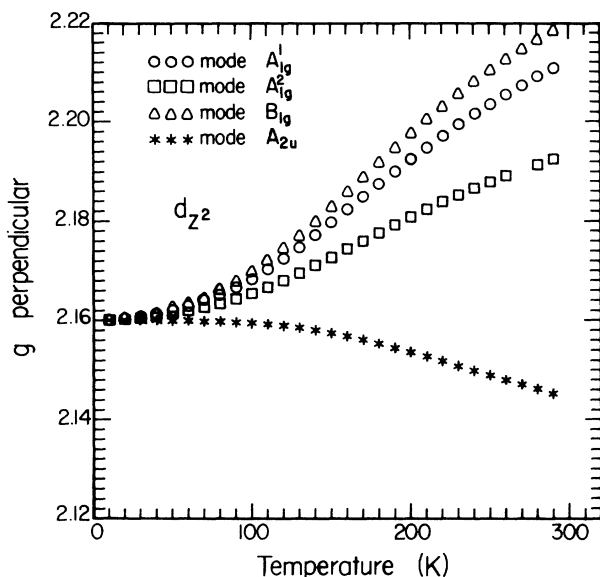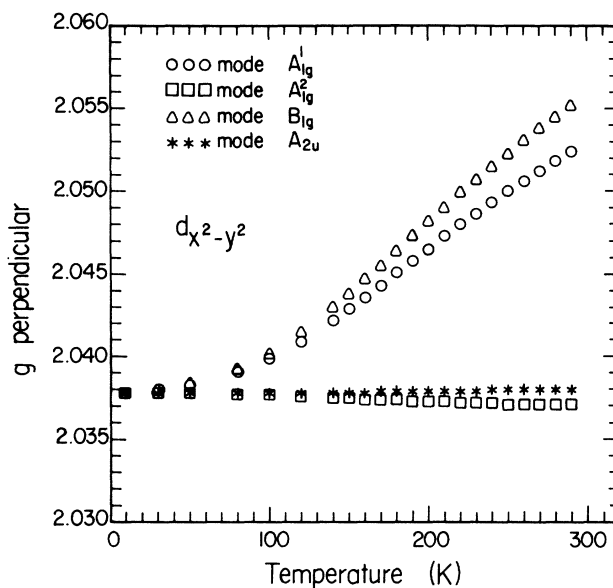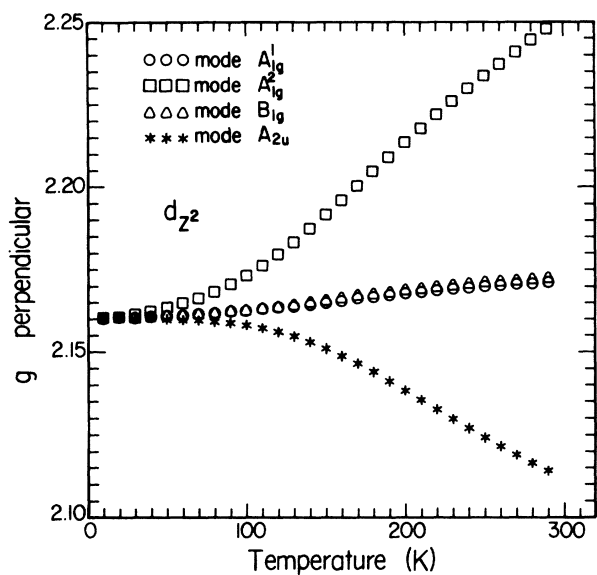
FIG. 3. Contribution of each stretching mode to the temperature dependence of the perpendicular component of the g tensor, d_{z^2} ground state. The frequency is assumed to be 50 cm^{-1} and the dissociation energy 500 cm^{-1}. Top: distance metal to axial ligand equal to the distance metal to equatorial ligand at $T=0$ K, taken as 2 Å. Bottom: distances equal to 3 and 2 Å, respectively.

FIG. 4. Contribution of each stretching mode to the temperature dependence of the perpendicular (top) and parallel (bottom) component of the g tensor, $d_{x^2-y^2}$ ground state. The frequency is assumed to be 50 cm^{-1} and dissociation energy 500 cm^{-1}. Considerations on the intramolecular distances at $T=0$ K, as made in Fig. 3, do not affect considerably this case.

TABLE I. Best-fitting data for the $3d^7$ and $3d^9$ species.

Species	Mode	Frequency[a]	Dissociation[a]	Anharmonicity
$[Ni(CN)_4Cl_2]^{3-}$, d_{z^2}	A_{1g}^1	92	1333	0.017
$[Ni(CN)_4Cl_2]^{5-}$, $d_{x^2-y^2}$	A_{1g}^1	69	810	0.021
	B_{1g}	194	725	0.067

[a]Estimated uncertainties are about 10%. Frequencies and dissociation energies are given in cm^{-1} units.
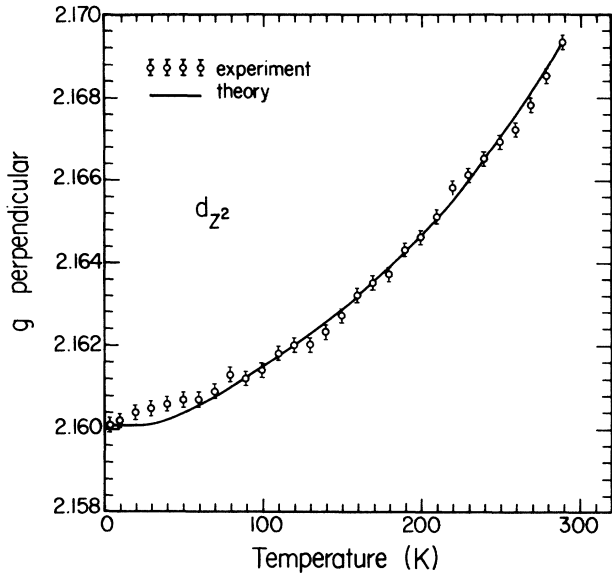
FIG. 5. Comparison between the EPR measurements at 9.3 GHz for [Ni(CN)$_4$Cl$_2$]$^{3-}$, d_{z^2} ground state, and theoretical values calculated with the best-fitting data displayed in Table I. The parallel component of the g tensor does not depend on the temperature, within the experimental accuracy.

unpaired electron lies in the equatorial plane ($d_{x^2-y^2}$ ground orbital and modes A_{1g}^1 and B_{1g}). When the unpaired electron occupies a d_{z^2} orbital, the probably higher vibration frequency of mode B_{1g} gives a good fitting when considering only an A_{1g}^1 mode. On the other hand, the calculated anharmonicity parameters are rather similar to those reported by Morse[15] for diatomic molecules.

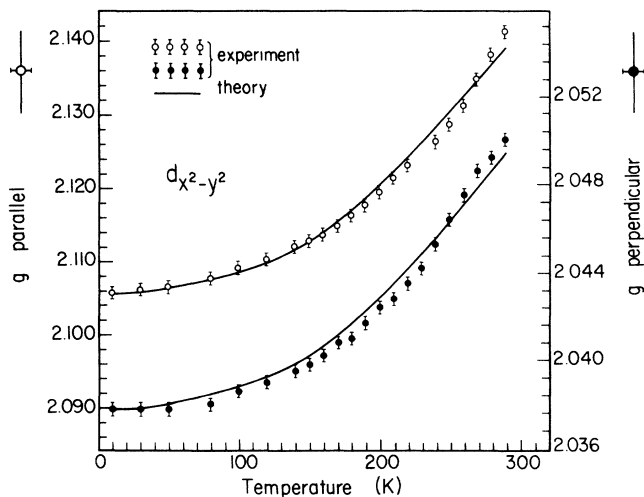In summary, we have shown that localized anharmonic

FIG. 6. Comparison between the EPR measurements for [Ni(CN)$_4$Cl$_2$]$^{5-}$, $d_{x^2-y^2}$ ground state, and theoretical values calculated with the best-fitting data displayed in Table I. The measurements were performed rigorously at the same experimental conditions used to obtain the data shown in Fig. 5. Solid circles correspond to the perpendicular component of the g tensor and open circles to the parallel component of the g tensor.

vibrations are related to temperature effects observed with electron paramagnetic resonance spectroscopy. This indicates that, in several cases, the dynamic Jahn-Teller effect does not apply. This effect should be used only if one can rule out the contribution to the temperature dependence on EPR data that arises from localized anharmonic vibration modes.

APPENDIX

In this appendix the C_{2v} crystal-field eigenfunctions and energies are listed. The intramolecular distances a, b, and c are shown in Fig. 1:

$$\varphi_1(A_1) = \cos\gamma \, d_{x^2-y^2} - \sin\gamma \, d_{z^2} \ ,$$

$$E_1 = X + W + \frac{4K^2}{G} - \left[G + \frac{8K^2}{G}\right]\sin^2\gamma \ , \tag{A1}$$

$$\varphi_2(A_1) = \cos\gamma \, d_{z^2} - \sin\gamma \, d_{x^2-y^2} \ ,$$

$$E_2 = Y - \frac{4K^2}{G} + \left[G + \frac{8K^2}{G}\right]\sin^2\gamma \ , \tag{A2}$$

$$\varphi(A_2) = d_{xy} \ ,$$

$$E_{xy} = X - W \ , \tag{A3}$$

$$\varphi(B_1) = d_{xz} \ ,$$

$$E_{xz} = L + J \ , \tag{A4}$$

$$\varphi(B_2) = d_{yz} \ ,$$

$$E_{yz} = L - J \ , \tag{A5}$$

where

$$X = 2\left[\frac{1}{a^3} + \frac{1}{b^3} - \frac{1}{c^3} - \frac{1}{f^3}\right]$$
$$+ \frac{R}{12}\left[\frac{4}{c^5} + \frac{4}{f^5} + \frac{3}{b^5} + \frac{3}{a^5}\right] \ ,$$

$$W = \tfrac{35}{12}R\left[\frac{1}{a^5} + \frac{1}{b^5}\right] \ ,$$

$$K = \sqrt{6}\left[\frac{1}{b^3} - \frac{1}{a^3}\right] + \frac{\sqrt{150}}{12}R\left[\frac{1}{b^5} - \frac{1}{a^5}\right] \ ,$$

$$Y = 2\left[\frac{1}{c^3} + \frac{1}{f^3} - \frac{1}{a^3} - \frac{1}{b^3}\right]$$
$$+ \tfrac{1}{2}R\left[\frac{4}{c^5} + \frac{4}{f^5} + \frac{3}{b^5} + \frac{3}{a^5}\right] \ ,$$

$$G = X + W - Y \ ,$$

$$\tan 2\gamma = \frac{2\sqrt{2}}{G} K \ ,$$

$$J = 3 \left[\frac{1}{a^3} - \frac{1}{b^3} \right] + \tfrac{35}{3} R \left[\frac{1}{b^5} - \frac{1}{a^5} \right] \ ,$$

and

$$L = \left[\frac{1}{c^3} + \frac{1}{f^3} - \frac{1}{a^3} - \frac{1}{b^3} \right]$$

$$- \tfrac{1}{3} R \left[\frac{4}{c^5} + \frac{4}{f^5} + \frac{3}{b^5} + \frac{3}{a^5} \right] \ .$$

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