



On the temperature dependence of the exchange interaction  
by Craig Edward Zaspel

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF  
PHILOSOPHY in Physics  
Montana State University  
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Abstract:

By assuming an anharmonic intermolecular potential for lattice displacement and an exponential form for the exchange energy, the exchange interaction is shown to be temperature dependent in the paramagnetic region. Bond strengths are taken from known tabulated results and overlap integrals are calculated with Slater-type orbitals so there are no adjustable parameters. Agreement with experimental results of  $K_2CuCl_4 \cdot H_2O$  and other layered compounds is shown.

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## ABSTRACT

By assuming an anharmonic intermolecular potential for lattice displacement and an exponential form for the exchange energy, the exchange interaction is shown to be temperature dependent in the paramagnetic region. Bond strengths are taken from known tabulated results and overlap integrals are calculated with Slater-type orbitals so there are no adjustable parameters. Agreement with experimental results of  $K_2CuCl_4 \cdot H_2O$  and other layered compounds is shown.

## I. AN HISTORICAL INTRODUCTION TO MAGNETISM

The aligning force in magnets was known since the beginning of recorded history, but it was not until the advent of quantum mechanics approximately two thousand years later that this phenomenon was understood. There were numerous attempts to explain magnetism; however, they all relied on some mystical power inherent in the magnet. Theories of the 17<sup>th</sup> and 18<sup>th</sup> centuries were related to the ancient Greek theory of magnetic forces. Epicurus'<sup>1</sup> explanation relied on the assumption that a magnet had a stream of "seeds" emanating from itself, and attraction was the result of interaction between the seeds and the air around a magnet. The Epicurean theory was not improved until 1644 when Descartes<sup>2</sup> published Principia Philosophiae. Descartes' theory was somewhat similar, except the particles streaming from the magnet were shaped like screws and they originated from pores near the poles. Since magnets exhibit both attraction and repulsion, there had to be two types of particles--right and left hand screws, and two types of pores--right and left hand nuts. Attraction corresponded to a matched screw and nut, and repulsion corresponded to the interaction of a left hand screw with a right hand nut. This was able to explain all magnetic effects at the time. The state of magnetism before quantum mechanics can best be described by Joyce:<sup>3</sup>



Universally that person's acumen is esteemed very little perceptive concerning whatsoever matters are being held as most profitable by mortals with sapience endowed to be studied who is ignorant of that which the most in doctrine erudited and certainly by reason of that in them high mind's ornament deserving of veneration constantly maintain when by general consent they affirm that other circumstances being equal by no exterior splendour is the prosperity of a nation more efficaciously asserted than by the measure of how far forward may have progressed the tribute of its solicitude for that proliferent continuance which of evils the original if it be absent when fortunately present constitutes the certain sign of ommipollent mature's incorrupted benefaction.

There was some progress phenomenologically. Weiss<sup>4</sup> introduced the molecular field or "Weiss" field to explain temperature dependence of the susceptibility. However, the origin of the field remained a mystery until the discovery of electron spin and the Pauli exclusion principle. Finally Heisenberg<sup>5</sup> applied quantum mechanics to the problem of ferromagnetism and showed that the exchange energy was responsible for magnetic coupling instead of seeds or screws.

The exchange interaction in systems of Fermions is an effect that does not have a analog in classical physics; it comes about from the indistinguishability of Fermions and the Pauli principle. To illustrate the origin of the exchange energy, we will consider two similar atoms A and B separated by a distance R. Using an approach similar to the Heitler-London theory of chemical bonding,<sup>6</sup> the two-electron wavefunction can be written as the antisymmetrized product of one-electron functions. The one-electron wavefunction is the product of an atomic orbital,  $\psi_A$  or  $\psi_B$  for atoms A and B,

and a spin function,  $\alpha$  or  $\beta$  for spin up and down. It can easily be shown that the properly antisymmetrized two-electron wavefunctions are:

$$\psi_1 = \frac{1}{\sqrt{2(1-S^2)}} \left\{ \varphi_A(x_1)\varphi_B(x_2) - \varphi_A(x_2)\varphi_B(x_1) \right\} \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \end{cases}$$

$$\psi_4 = \frac{1}{\sqrt{2(1+S^2)}} \left\{ \varphi_A(x_1)\varphi_B(x_2) + \varphi_A(x_2)\varphi_B(x_1) \right\} (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

where  $x_1$  and  $x_2$  are the coordinates of electrons 1 and 2. Next these states will be used to calculate the energy for the two-electron system with the Hamiltonian:

$$H = H_1 + H_2 + H_{12}$$

Here  $H_1$  and  $H_2$  are the one-electron terms, and  $H_{12}$  is the electron-electron interaction.  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  are degenerate; these three states have energy:

$$E_t = \frac{1}{2(1-S^2)} \left\{ 2 \langle \varphi_A(1)\varphi_B(2) | H | \varphi_A(1)\varphi_B(2) \rangle - 2 \langle \varphi_A(1)\varphi_B(2) | H | \varphi_B(1)\varphi_A(2) \rangle \right\}$$

The other state is a singlet with energy:

$$E_s = \frac{1}{2(1+S^2)} \left\{ 2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle \right. \\ \left. + 2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle \right\}.$$

Here,  $S$  is the overlap integral, defined by:

$$S = \int \varphi_A(x) \varphi_B(R+x) dx.$$

For reasons which will be immediately apparent, the exchange energy is defined as the difference between the triplet and singlet state energies:

$$E_{ex} = E_t - E_s$$

For the two-electron system this difference is

$$E_{ex} = \frac{1}{1-S^4} \left\{ S^2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle \right. \\ \left. - \langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle \right\}.$$

This can be further simplified by explicitly using the one and two-electron parts of the Hamiltonian in the first term above. Now there are terms like

$$\langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle$$

and the integration over the coordinates of electron 2 is trivial; the expression becomes:

$$S \langle \varphi_A(1) | H_1 | \varphi_B(1) \rangle.$$

Doing the same for  $H_2$ , the exchange energy is

$$E_{ex} = \frac{2}{1-S^2} \left\{ - \langle \varphi_A(1) \varphi_B(2) | H_{12} | \varphi_B(1) \varphi_A(2) \rangle - 2S \langle \varphi_A(1) | H_1 | \varphi_B(1) \rangle + S^2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle \right\}.$$

It is now obvious why the above definition was used for the exchange energy; if we had used orthogonal orbitals, the exchange energy

reduces to the ordinary exchange integral

$$E_{ex} = -2J \quad J \equiv \langle \psi_A(1)\psi_B(2) | H_{12} | \psi_B(1)\psi_A(2) \rangle.$$

For this case, Dirac<sup>7</sup> showed that the exchange energy depends only on the relative spin orientations and the exchange Hamiltonian could be expressed as a product of spin functions:

$$E_{ex} = -2J \vec{S}_1 \cdot \vec{S}_2.$$

Now we can extend the spin Hamiltonian to the more general problem of nonorthogonal orbitals by defining the exchange constant

$$-J = E_t - E_s$$

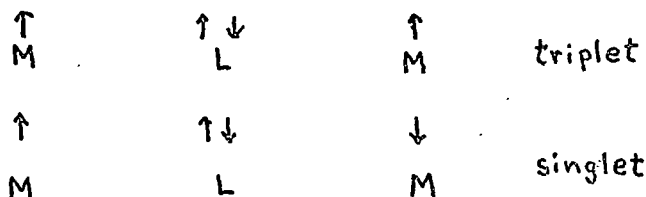
which is the complicated expression that was calculated earlier, and we arrive at the Heisenberg-Dirac-Van Vleck Hamiltonian:

$$H_{ex} = -J \vec{S}_i \cdot \vec{S}_j.$$

Certain observations can be made concerning the sign of  $J$  and the magnetic behavior of our two-electron system. First, if  $J$  is positive, the parallel spin arrangement will have lower energy; this corresponds to ferromagnetism. For  $J$  negative, the antiferromagnetic state will have lower energy. So at least in principle, we can

predict whether a system will be ferromagnetic or antiferromagnetic by calculating  $E_s - E_t$ . For our two-electron problem, the first term is the ordinary exchange integral; since this is just the self-energy of the overlap charge distribution, the first term in the expression for  $J$  is positive. The second term is related to the energy of a single electron bound state, which is negative. The last term can go either way. So even for this simple two-electron system it is very difficult to predict the sign of  $J$  because each term in  $H_{ex}$  is usually large compared to  $J$ , and there is a delicate balance that can go either positive or negative.

Most magnetic systems are considerably more complicated than the previous two-electron problem; usually there is a diamagnetic ligand between the paramagnetic atoms, and the ligand electrons must also be included in the calculation of triplet and singlet state energies. This particular three atom problem is known as superexchange because the magnetic electrons interact over relatively large distances. The exchange constant for superexchange is still the difference between singlet and triplet states; however, the triplet and singlet spin configurations are illustrated below.



It is now necessary to find the energy of both spin configurations, which defines the exchange constant. The calculation is similar to the earlier example except it is a four electron problem, which becomes an immense complication. The most refined calculations of the exchange constant use molecular orbitals for the one-electron functions, and electron correlation is taken into consideration through configuration interaction. But even in these calculations all that can be hoped for is the correct sign for  $J$ , so the exchange constant is usually experimentally determined.

When the exchange constant is measured by different methods, which will be discussed later, the possibility that  $J$  may be temperature dependent is ignored. The remaining chapters will deal with temperature dependence of the exchange energy. First, experimental methods for measuring the exchange energy will be discussed. The next chapter presents experimental evidence which indicates that the exchange energy is temperature dependent. The final chapters investigate possible mechanisms contributing to the temperature dependence; the theoretical results will then be compared with the experiments presented earlier. The mechanism of primary concern in this work is phonon modulation of the exchange integral. A development of the model for this mechanism comprises chapter five.

## II. EXPERIMENTAL DETERMINATION OF THE EXCHANGE ENERGY

All cooperative magnetic properties are determined by the sign and magnitude of  $J$ ; epr linewidths, spin-wave dispersion relations, low temperature specific heat, or any other parameter related to cooperative magnetic phenomenon. Therefore,  $J$  has to be determined (either experimentally or theoretically) in order to compare magnetic measurements with the Dirac-Heisenberg theory. The exchange constant can be calculated using molecular orbital theory; however, as noted in the introduction, this is very difficult and inaccurate--very much like poorly convergent perturbation theory. For all practical purposes  $J$  is determined experimentally from any kind of cooperative magnetic effect. Three methods that are used most often are: low temperature specific heat, susceptibility measurements, and epr linewidth measurements.

### A. Spin-wave Specific Heat

Since spin-wave modes are the main contribution to the low temperature specific heat, the expression for the specific heat,  $C_v$ , contains  $J$  explicitly. The spin-wave contribution to  $C_v$  is:

$$C_v = \frac{\partial}{\partial T} \sum_k \hbar \omega_k \langle n_k \rangle ,$$



$\omega_k$  is obtained from the spin-wave dispersion relation and  $\langle n_k \rangle$  is the Bose-Einstein distribution. Employing the following three approximations:  $k$  is small, the only spin-spin interaction is expressed as the Heisenberg Hamiltonian, and the sum is converted to an integral over  $k$ ; it can straightforwardly be shown that the specific heat is<sup>9</sup>:

$$C_v = \frac{15}{4} \zeta\left(\frac{5}{2}\right) k_B \left( \frac{k_B}{4\pi J S a^2} \right)^{3/2} T^{3/2}$$

for a simple cubic lattice with lattice constant  $a$ . This method is useful for determination of  $J$  in the low temperature region,  $T < T_c$ , because spin-wave excitations are the main contribution to the specific heat.

#### B. Curie and Neel Temperature

A method to directly obtain  $J$  is the determination of the Weiss temperature for ferromagnets or the Neel temperature for antiferromagnets. The Weiss Temperature  $\Theta$  is defined by the Curie-Weiss law for temperature dependence of the susceptibility.<sup>9</sup>

$$\chi = \frac{C}{T - \Theta}$$

where  $C$  is a constant,  $z$  is the number of nearest neighbors and

$$\Theta = \frac{S(S+1)}{3k_B} z J.$$

Thus  $J$  can be obtained from the intercept of a  $\chi^{-1}$  vs  $T$  curve.

Similarly, for an antiferromagnet, the susceptibility is given by<sup>9</sup> :

$$\chi = \frac{C}{T + T_N}$$

where  $T_N = \frac{|J|S(S+1)}{3K_B} Z$ .

### C. EPR Linewidths

#### 1) Spin-Spin Interaction

We can get  $J$  for high temperature from the width of exchange narrowed epr lines. The two interesting cases are: the effect of exchange on the relative separation of two resolved resonance lines with different  $g$  values, and exchange narrowing of a single resonance line. The first case has been treated by Anderson<sup>10</sup> for two lines symmetrically spaced  $\pm \omega_0$  from an arbitrary center. The exchange interaction tends to bring two lines together, and the shift from  $\omega_0$  is given by:

$$\Delta\omega = \pm \omega_e \sqrt{\frac{\omega_0^2}{\omega_e^2} - 1}$$

If  $\omega_0$  can be determined from a preferred orientation of the external field, then the exchange energy,  $J \approx \hbar \omega_e$  can be obtained from a measurement of  $\Delta\omega$ . This method was used to obtain  $J$  for the compound  $K_2CuCl_4 \cdot 2H_2O$ , which will be discussed in the next chapter.

The effect of  $J$  on the width of a single line can be illustrated by the following problem: Consider an array of spins in an external magnetic field; the Hamiltonian is expressed as three terms:

$$H = H_z + H_d + H_e,$$

where each term is defined by

$$H_z = g\beta H \sum_i S_i^z$$

$$H_d = \sum_{i>j} \frac{g^2\beta^2}{r_{ij}^3} \left\{ \vec{S}_i \cdot \vec{S}_j - 3(\vec{S}_i \cdot \hat{r}_{ij})(\vec{S}_j \cdot \hat{r}_{ij}) \right\}$$

$$H_e = -J \sum \vec{S}_i \cdot \vec{S}_j.$$

The sum in  $H_e$  is over nearest neighbor pairs. An external field of the form:

$$H_1^x \cos \omega t$$

will induce transitions between the Zeeman levels. For infinite temperature the absorption line for these transitions is given by the expression<sup>11</sup>:

$$I(\omega) = \int_{-\infty}^{\infty} \langle S_x(t) S_x(0) \rangle e^{i\omega t} dt,$$

and  $S_x(t)$  can be calculated from the Heisenberg equation,

$$i\hbar \frac{d}{dt} S_x = [H, S_x].$$

Since  $S_x$  commutes with the exchange Hamiltonian,  $H_e$  is not included explicitly in the equation of motion. However,  $H_e$  does not commute with  $H_d$ , and  $H_d$  has a time dependence given by:

$$i\hbar \frac{d}{dt} H_d = [H_{ex}, H_d] ,$$

or in other words, the dipole interaction is modulated by the exchange energy. Using an explicit form for the matrix element of  $H_d(t)$  and assuming  $\omega_e \gg \omega_d$ , Anderson and Weiss<sup>11</sup> have shown that the resonance linewidth is given approximately by:

$$\Delta\omega \propto \frac{\omega_d^2}{\omega_e}$$

where  $\omega_d^2$  is the second moment of the resonance line, and  $\omega_e = J/\hbar$

This expression for  $\Delta\omega$  can change by a factor of about 1.5 depending on how  $H_d$  is modulated by the exchange interaction.

To arrive at the above result for  $\Delta\omega$  it was assumed that  $\omega_e \gg \omega_d$  and the form of modulation was a Gaussian random function. As shown by Richards<sup>12</sup>, this is equivalent to assuming the spin correlation function has a time dependence

$$\langle S_x(t) S_x(0) \rangle \propto \cos \omega t e^{-t/\tau_2} ,$$

and evaluation of the integral for  $I(\omega)$  using this correlation function results in a Lorentzian lineshape given by

$$I(\omega) \sim \frac{\omega \Delta \omega}{(\omega - \omega_0)^2 + \Delta \omega^2}$$

where  $\omega_0 = g\beta H$ ,  $\Delta \omega = 1/\tau_2$ , and  $\tau_2$  is the spin-spin correlation time, or the lifetime of the excited Zeeman state. In the absence of a spin-lattice interaction, the exchange constant can be obtained from a knowledge of the epr linewidth and second moment. The temperature dependence of  $J$  may then be extracted from the linewidth at different temperatures.

It should also be mentioned that Kubo and Tomita<sup>13</sup> did a perturbation series expansion for the spin correlation function, and calculated the linewidth at finite temperature.

## 2) Spin-Lattice Interaction.

One contribution to the linewidth that was ignored because the spin-phonon interaction did not appear in the Hamiltonian is spin-lattice relaxation. There are many mechanisms--that will be considered later--which couple the spin system and the lattice, but as an example consider the Waller<sup>14</sup> process: A spin in the state  $M_S = \frac{1}{2}$  makes a transition to the  $M_S = -\frac{1}{2}$  state by interaction with a phonon of energy  $g\beta H$ . A transition rate  $W$  can be calculated and from this the lifetime of the  $M_S = \frac{1}{2}$  state is related to  $W$  by  $\tau = \frac{1}{W}$ .

What type of perturbations will cause spin flips? The exchange Hamiltonian commutes with  $S^z$ , so phonon modulation of  $J$  will not contribute to  $W$ . Next consider the dipole-dipole interaction:

$$H_0 = \sum_{i \neq j} \frac{g^2 \beta^2}{r_{ij}^3} (3 \cos^2 \theta_{ij} - 1) \left\{ \frac{1}{4} (S_i^+ S_j^- + S_i^- S_j^+) - S_i^z S_j^z \right\}$$

$$H_1 = \sum_{i \neq j} \frac{g^2 \beta^2}{r_{ij}^3} \frac{3}{2} \sin \theta_{ij} \cos \theta_{ij} \left\{ (S_i^z S_j^+ + S_i^+ S_j^z) e^{-i\phi_{ij}} + (S_i^z S_j^- + S_i^- S_j^z) e^{i\phi_{ij}} \right\}$$

$$H_2 = \sum_{i \neq j} \frac{g^2 \beta^2}{r_{ij}^3} \frac{3}{4} \sin^2 \theta_{ij} \left\{ S_i^+ S_j^+ e^{-2i\phi_{ij}} + S_i^- S_j^- e^{2i\phi_{ij}} \right\}$$

$$H_d = H_0 + H_1 + H_2 .$$

The selection rules are  $\Delta M_s = 0$  for  $H_0$  which does not result in spin flips, whereas for  $H_1$  and  $H_2$   $\Delta M_s = \pm 1$  and  $\Delta M_s = \pm 2$ ; therefore, for this process a finite  $T_1$  is the result of modulation of  $H_1$  and  $H_2$ . It is interesting to note that when  $H_1$  and  $H_2$  are included in the spin-spin correlation function, the linewidth is increased by a factor of  $10/3$  which makes  $\Delta\omega$  agree much better with experimental linewidths. This mechanism for spin-lattice relaxation and the  $10/3$  effect<sup>11</sup> originate from the same Hamiltonian; sometimes they

are even given the same name.

Two relaxation processes contribute to the observed linewidth: the spin-spin relaxation with its characteristic  $T_2$ , and the spin-lattice interaction which has a corresponding spin-lattice relaxation time,  $T_1$ . In order to extract  $J$  from the epr linewidth, it is necessary to determine how  $\Delta\omega$  depends on  $1/T_1$  and  $1/T_2$ . The simplest case has a characteristic bell-shaped resonance curve, and the widths are given approximately by  $\Delta\omega_1 \propto \frac{1}{T_1}$  and  $\Delta\omega_2 \propto \frac{1}{T_2}$ . Using the suggestion of Bloembergen, Purcell, and Pound<sup>15</sup>, the assumption will be made that the observed resonance line is the sum of two lines at  $\omega_0$ , each of which have widths  $\Delta\omega_1$  and  $\Delta\omega_2$ . The resulting line,  $Y(\omega)$ , not necessarily Gaussian, is:

$$Y(\omega) = I_1 \exp\left\{-\ln 2 \left(\frac{\omega - \omega_0}{\Delta\omega_1/2}\right)^2\right\} + I_2 \exp\left\{-\ln 2 \left(\frac{\omega - \omega_0}{\Delta\omega_2/2}\right)^2\right\}.$$

The width of  $Y(\omega)$  is obtained from the expression relating the linewidth and the second moment--  $\Delta\omega^2 \propto c \langle \omega^2 \rangle$ <sup>16</sup>;  $c$  is a constant that depends on the particular lineshape,  $\langle \omega^2 \rangle$  is the second moment of  $Y(\omega)$  given by:

$$\langle \omega^2 \rangle = \frac{1}{A} \int_{-\infty}^{\infty} (\omega - \omega_0)^2 Y(\omega) d\omega$$

where  $A$  is the area under the resonance line:

$$A = \int_{-\infty}^{\infty} Y(\omega) d\omega.$$

The integration can easily be done and the linewidth for both relaxation mechanisms is:

$$\Delta\omega \sim \sqrt{\Delta\omega_1^2 + \Delta\omega_2^2} - \Delta\omega_1 \Delta\omega_2.$$

If  $T_1 \gg T_2$ ,  $\Delta\omega$  is approximately:

$$\Delta\omega \approx \frac{1}{T_2} + \frac{1}{2T_1}$$

and frequently the second term can be neglected completely so  $J$  is obtained in that case from the results of reference (10).

For the case when  $T_1$  is not large, different spin-lattice relaxation mechanisms besides the Waller process must be looked at. A very good review of different mechanisms is given in reference (16), and each will be considered briefly here.

The Waller process results in a relaxation time given by  $\frac{1}{T_1} \sim H^2 T$ . A typical  $T_1$  is 10 sec, and a typical  $T_2$  is  $10^{-9}$  sec so this process is too long to contribute to the linewidth.

Next consider a spin-phonon collision where the energy loss of a phonon is  $g\beta H$ . This is the two-phonon Raman process which



was also treated by Waller<sup>14</sup> in 1932. The temperature dependence of  $T_1$  can be obtained for two cases. For low temperatures,  $k_B T \ll \hbar \omega_0$ , and  $\frac{1}{T_1} \sim T^7$ ; for high temperature,  $k_B T \gg \hbar \omega_0$ , and  $\frac{1}{T_1} \sim T^2$ .

A typical  $\Theta_0$  is 100°K so  $1/T_1$  usually goes as something between  $T^7$  and  $T^2$  for this process. In the high temperature approximation,  $T_1$  is still about 10 sec at 300°K which is still much greater than  $T_2$ .

A shorter  $T_1$  can come from modulation of the ligand field<sup>17</sup> which sets up an oscillating electric field as a perturbation. This perturbation will only have a direct effect on the crystal field splitting of orbital states, and the spin-phonon coupling is a second order effect that comes from spin-orbit coupling. For the one-phonon direct process non-Kramers and Kramers ions, which have integral and half-integral spin respectively, are investigated separately. The ground state of a non-Kramers ion can split in a crystalline field of low enough symmetry. Modulation of the Stark field then affects the spin through the spin-orbit interaction. With appropriate calculations, the relaxation time is shown to have a field and temperature dependence<sup>17</sup>:

$$\frac{1}{T_1} \sim H^2 T.$$

At first glance it appears as if phonon modulation will not affect the ground state of a Kramers ion. However, Kronig<sup>18</sup> has shown that there are matrix elements due to the interaction of the Kramers state and the Stark field in the presence of an external magnetic field. For this case:

$$\frac{1}{T_1} \sim H^4 T.$$

A non-Kramers ion will have a  $T_1$  of about  $10^{-3}$  sec and a Kramers ion has a  $T_1$  of 1 sec for this process, which is still long compared to  $T_2$ .

In 1961 Orbach<sup>19</sup> was able to account for the anomalously short relaxation times by a process that is essentially an indirect transition between two Kramers states.

