Binuclear unit $(Ti_2Cl_9)^{3-}$: A new development for the exchange between orbitally unquenched ions

M. Drillon

Departement Science des Materiaux, Ecole Nationale Supérieure de Chimie, 1, rue Blaise Pascal, B.P. N. 296/R8, 67008 Strasbourg Cedex, France

R. Georges

Laboratoire de Physique du Solide, Université de Bordeaux I, 351, Cours de La Libération, 33405 Talence, France

The problem of exchange interaction between two Ti^{3+} (d^1) ions in a binuclear unit $(Ti_2Cl_9)^{3-}$ is investigated from a microscopic description of the exchange mechanisms. With the use of pseudofermion operators, the effective Hamiltonian between the orbitally degenerate ground terms $^2T_{2g}$ is determined with the various excited configurations being taken into account. Further, local trigonal distortion, spin-orbit coupling, and covalency effects are introduced for describing the real magnetic behavior of the entity. Thus it is shown that the use of the Heisenberg Hamiltonian for distorted systems is often a poor approximation. Lastly, a least-squares fitting of the experimental data of $Cs_3Ti_2Cl_9$ is proposed from the developed model.

A major part of the work on paramagnetic isolated entities reported in the literature is restricted to orbitally nondegenerate S-state ions.[1] In this case, all the more complex aspects of cooperative magnetic phenomena and interaction in presence of unquenched orbital angular contributions are irrelevant so that the problem may be solved exactly, at all temperatures, using a simple spin formalism as suggested by Kambe.[2]

Contrastingly, when the interacting ions exhibit an orbital degeneracy in their ground state the spins are strongly correlated to the orbital moments and this approach is no longer valid. All configurations for each single site must be considered; this increases the difficulty of the task of determining the exchange Hamiltonian whose general form has already been discussed in several theoretical papers.[3-11] In particular, attempts have been made to establish the empirical Hamiltonian, but it is not always easy, through the proposed approaches, to give physical meanings to the parameters which could be deduced experimentally.

In a previous study, we have reinvestigated this problem for the $^2T_2$ and $^3T_1$ ground-term systems in commonly observed molecular arrangements (of D_{2h}, D_{3h}, or D_{4h} symmetry).[12] Starting with Anderson's formalism,[13] we have defined a new expression for the Hamiltonian which takes into account the energy difference between the various spin configurations in the polarized states; this aspect had been ignored until now. In particular, it was shown that predictions concerning even the sign of the spin-spin coupling may strongly depend on an accurate knowledge of excited configuration and local distortion energies. This is the reason why Goodenough's model,[14] which provides a useful basis for qualitative interpretations concerning the interactions, is often deficient when orbitally degenerate ions are involved.

The purpose of the present paper is to check the validity of our model on real compounds where the interacting ions are two Ti^{3+} linked by three bridging ligands; this is the case of $(Et_2NH_2)_3Ti_2Cl_9$,[15,16] $Cs_3Ti_2Cl_9$,[17,18] and $Cs_3Ti_2Br_9$[19] whose properties have already given rise to conflicting interpretations. Among these, we shall mention the study of Briat *et al.*[18] which is the only one to our knowledge which has been developed from single-crystal measurements. The fact that these compounds may be described in terms of well-isolated binuclear units $(Ti_2Cl_9)^{3-}$, thus avoiding statistical approximations, is undoubtedly accountable for this interest.

I. STRUCTURE AND MAGNETIC PROPERTIES

The crystal structure of $Cs_3Ti_2Cl_9$ is isomorphous with that of $Cs_3Cr_2Cl_9$ determined by

Wessel and Ijdo.[19] It corresponds to the hexagonal symmetry $P6_3/mmc$ with the cell dimensions $a = 7.32$ Å and $c = 17.97$ Å. In the molecular arrangement each Ti^{3+} ion, octahedrally surrounded by Cl^- ligands, is connected to another one in order to form binuclear units $(Ti_2Cl_9)^{-3}$ along the c axis. These units may be schematized as two octahedra sharing a face so that they show the D_{3h} symmetry. Further, they are well separated in the space since the shortest Ti^{3+}-Ti^{3+} distance between neighboring units is about 7.20 Å while it is 3.10 Å within each unit. Consequently, the magnetic behavior will be considered as resulting from an assembly of noncoupled binuclear entities. The temperature dependence of the susceptibility has been measured in the range 4.2 − 320 K by Briat *et al.*[18]

At first, it may be noticed that the susceptibility is highly anisotropic, the threefold axis which contains the two centers appearing to play a special role; the susceptibility measured along this direction $(\chi_{\parallel})$ is lower than any perpendicular one $(\chi_{\perp})$. After correcting for the contributions of impurities which alter the behavior at very low temperatures it is shown they both decrease when cooling down to about 150 K and remain constant at lower temperatures. The anisotropy $\Delta\chi$ is then equal to 540×10^{-6} cm^3 mol^{-1}.

Finally, these data are consistent with antiferromagnetic binuclear entities as was expected from molecular structure. Related studies on $(Et_2NH_2)_3Ti_2Cl_9$ [16,20] lead to similar conclusions.

The anisotropy measurements reveal the importance of the local distortions from the octahedral symmetry of the environment around each Ti^{3+} ion. Furthermore, the binuclear units cannot be adequately described by a simple spin formalism; the exchange interaction not only depends on the spin moments of the intervening ions but also on the orbital ones.

In accordance with our previous paper,[12] we now develop a theoretical approach to this problem; the specific case of $Cs_3Ti_2Cl_9$ is taken up in the last section.

II. INTERACTION BETWEEN $^2T_{2g}$ SINGLE-ION GROUND STATES

Let us consider a given entity built from two slightly distorted octahedral sites sharing a face with the overall symmetry D_{3h}. We assume for each site a t_{2g}^2 electronic structure corresponding to a $^2T_{2g}$ ground term.

In the absence of exchange interaction between the sites labeled i and j, the entity behaves as two nonconnected $^2T_{2g}$ ions; the magnetic moment depends on spin-orbit coupling and trigonal distortions. The calculations have been performed by Figgis, who also took into account the covalence of metal−ligand bonds.[21,22]

Let us now introduce the effects of an exchange interaction between the magnetic sites. A practical method for describing this contribution consists of starting from Anderson's Hamiltonian[13]

$$\mathcal{H} = \mathcal{H}_{ij} + \mathcal{H}_{ji} = \sum_{mm'}\sum_{\sigma}[b_{mm'}C^*_{m\sigma}(i)C_{m'\sigma}(j) + b_{m'm}C^*_{m'\sigma}(j)C_{m\sigma}(i)] , \tag{1}$$

which accounts for the electronic transfers of the $i \rightarrow j$ or $j \rightarrow i$ type. The $C^*_{m\sigma}$ and $C_{m\sigma}$ are anticommuting operators which, respectively, create and annihilate particles on an orthonormal set of states $|m\sigma\rangle$. $b_{mm'}$ stands for the transfer integrals between the orbitals m and m'. These integrals couple unpolarized states (corresponding to the equipartition of the electrons among all sites) to the polarized ones so that the energy of the system is lowered.

As shown in our previous paper,[12] two kinds of polarized states are involved, assuming that spin-spin intraionic coupling is large compared to the l-l or l-s one. Specifically in the present case, an operator such as $C^*_{m\sigma}(i)C_{m'\sigma}(j)$ gives rise to two-electron states on site i, belonging to either $^3T_1$ $(S = 1)$ or $^1A_1 + ^1E_2 + ^1T_2$ $(S = 0)$ representations; these two sets are well separated in energy (Hund's rule). The effective Hamiltonian resulting from second-order perturbations must be written as

$$\mathcal{H} = -\sum_{\alpha}\frac{\mathcal{H}_{ij}|\psi_e^{\alpha}\rangle\langle\psi_e^{\alpha}|\mathcal{H}_{ji}}{U_e^{\alpha}} - \sum_{\beta}\frac{\mathcal{H}_{ji}|\psi_e^{\beta}\rangle\langle\psi_e^{\beta}|\mathcal{H}_{ij}}{U_e^{\beta}} , \tag{2}$$

where $|\psi_e^{\alpha}\rangle$ and $|\psi_e^{\beta}\rangle$ are polarized states resulting from $i \rightarrow j$ and $j \rightarrow i$ electron transfers, respectively, with U_e^{α} and U_e^{β} being the corresponding energies. These essentially depend on polarization effects and spin-spin intraionic couplings.

For a symmetrical pair of identical cations allowing us to ignore the distinction between U_e^α and U_e^β, we have

$$U_e^\alpha = U_e^\beta = U_e^a + \langle \psi_e^\alpha \mid \mathscr{H}^s \mid \psi_e^\alpha \rangle . \tag{3}$$

Finally, defining collective excited states from total spin quantum numbers on each site, $\mid S_i S_{iz} \rangle \mid S_j S_{jz} \rangle$, we get

$$\mathscr{H} = -\sum_{\substack{mm' \\ nn'}} \sum_{\sigma\zeta} \sum_{S_i S_{iz}} \sum_{S_j S_{jz}} \frac{b_{mm'} b_{n'n}}{U_e^a + U^s(S_i S_j)} \langle C_{m\sigma}^* \mid S_i S_{iz} \rangle \langle S_i S_{iz} \mid C_{n\zeta} C_{m'\sigma} \mid S_j S_{jz} \rangle \langle S_j S_{jz} \mid C_{n'\zeta}^* \rangle + \mathscr{H}_{\text{sym}} \tag{4}$$

with $\mathscr{H}_{\text{sym}}$ standing for the symmetrical part of the Hamiltonian obtained by interchanging the subscripts i and j. Such an expression differs from the generally encountered ones by the distinction introduced between the various excitation terms. It results in a tricky but much more convenient expression when developing the single-ion operators $C_{m\sigma}^* \mid S_i S_{iz} \rangle \langle S_i S_{iz} \mid C_{n\zeta}$ occurring in (4) in terms of spin and orbital components.

At first sight, the result of this approach strictly includes the kinetic contribution in terms of Anderson. Any rigorous extension would have to take into account the self-energy of the overlap charges between partly occupied orbitals on adjacent atoms, namely the potential exchange.

Actually it may be shown that this does not modify the general form of the Hamiltonian. We have only to introduce in the constant an additional term

$$J_{\text{potential}} = \left\langle \psi_i(1)\psi_j(2) \left| \frac{e^2}{r_{12}} \right| \psi_i(2)\psi_j(1) \right\rangle , \tag{5}$$

which is always positive. It is generally negligible but may be important when the orbitals located on adjacent sites are orthogonal; such a configuration may be observed in heterobinuclear entities.[23] In the case we are concerned with it can be readily neglected.

At this stage of the investigation, let us examine the transfer integrals playing an effective role within the exchange interaction. Two models referred to as I and II may be developed:

(I) Considering only the t_{2g} orbitals involved in the present system, we assume, in a first step, the overlaps $\langle xy \mid yz \rangle$, $\langle xy \mid zx \rangle$, and $\langle yz \mid zx \rangle$ between nonequivalent orbitals to be very small and we neglect the corresponding transfer integrals (Fig. 1). By contrast, the mechanisms involving similar orbitals on both cations give rise to significant contributions. They are of direct or superexchange type; however, it is not useful in the present context to distinguish these contributions

and we shall mix them into effective parameters J_1 and J_2 defined by

$$J_1 = \frac{b^2}{U_e^a + U^s(0,0)}, \quad J_2 = \frac{b^2}{U_e^a + U^s(1,0)} , \tag{6}$$

where b stands for the three identical integrals $b_{xy,xy}$, $b_{yz,yz}$, and $b_{zx,zx}$, and $U^s(0,0)$ and $U^s(1,0)$ refer, respectively, to $S = 0$ and $S = 1$ spin configurations in the t_{2g}^2 manifold.

(II) The second approach does take into account the previously neglected contribution arising from nonequivalent orbitals. This results in an exchange anisotropy (see Appendix) and the useful parameters are now of the form $(b^2/U)(1-\eta)^2$, $(b^2/U)(1 + 2\eta)^2$, and $(b^2/U)(1-\eta)(1+2\eta)$, where U represents $U_e^a + U^s(0,0)$ or $U_e^a + U^s(1,0)$. Since η should be small we can neglect any η^2 contributions and the Hamiltonian may then be written as

$$\mathscr{H}_{\text{II}} = \mathscr{H}_1 + \eta \mathscr{H}' ,$$

where $\mathscr{H}_1$ refers to model I and $\mathscr{H}'$ is the first-order η contribution. In fact, when we are concerned with practical problems it is essential to remember that this last term acts as a small perturbation. Freeman and Watson[24] have shown that exchange integrals for differently orientated orbitals, contributing to $\mathscr{H}'$, are 2 orders of magnitude

$\langle XZ \mid XZ \rangle = a$ $\langle XZ \mid YZ \rangle = \eta a$ $\langle XZ \mid XY \rangle = \eta a$
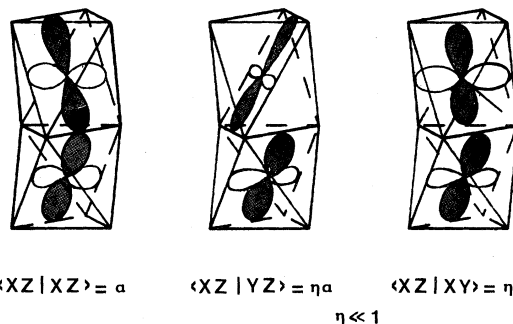
$\eta \ll 1$

FIG. 1. Comparison between the various orbital configurations and the respective overlap integrals in a binuclear entity of D_{3h} symmetry.

smaller than the integrals for similar ones. Thus, we have to consider further important effects such as the local site distortion, the spin-orbit coupling, and, equally, the electron delocalization toward the ligands resulting in an orbital reduction factor. Thus, the system may appear to be overparametrized to describe a set of magnetic data; in the absence of optical measurements it would be more realistic to let only J_1 and J_2 be the adjustable exchange parameters. Such a procedure is applied in the following discussion of a t_{2g}^1-t_{2g}^1 system.

III. MAGNETIC PROPERTIES OF A t_{2g}^1-t_{2g}^1 ENTITY

By taking $\eta = 0$, expression (4) only involves terms of the form

$$C_{m\sigma}^* \mid S_i S_{iz} \rangle \langle S_i S_{iz} \mid C_{n\zeta} C_{m\sigma} \mid S_j S_{jz} \rangle \langle S_j S_{jz} \mid C_{n\zeta}^* \ ,$$

each one being multiplied by J_1 or J_2 according to the (S_i, S_j) pair under consideration. Using the possibility of describing the T states as eigenstates of a fictitious $L = 1$ orbital operator, we may express these quantities in terms of spin and orbital moment operators. A tedious though straightforward calculation thus leads to the result

$$\mathcal{H}_1 = -\tfrac{1}{2}J_1[1 - \vec{L}_1 \cdot \vec{L}_2 - (\vec{L}_1 \cdot \vec{L}_2)^2](1 + 4\vec{S}_1 \cdot \vec{S}_2)$$
$$+ \tfrac{1}{4}(J_1 - J_2)(1 - \vec{L}_1 \cdot \vec{L}_2)(2 + \vec{L}_1 \cdot \vec{L}_2)(3 + 4\vec{S}_1 \cdot \vec{S}_2) \ .$$

$$(7)$$

The first term of this operator describes the exchange when one neglects the intraionic spin-spin coupling while the second one precisely takes it

FIG. 2. Energy-level scheme given by Eq. (7) for a t_{2g}^1-t_{2g}^1 entity; comparison with the results of the Heisenberg and Anderson models.

into account.

Obviously, this Hamiltonian shows drastic differences with the Heisenberg expression; however, one can remark the isotropic character of the interaction clearly results from neglecting η. It was of interest to compare the results of this approach for $J_1 = J_2$ and $J_1 \neq J_2$ to those of the Heisenberg Hamiltonian. In this way, let us define a new set of parameters

$$J = \tfrac{1}{2}(J_1 + J_2), \quad J' = -\tfrac{1}{2}(J_1 - J_2) \ , \quad (8)$$

allowing us a direct comparison of the various models. From the respective energy diagrams (Fig. 2) the following points may be emphasized:

(i) The approximation $J' = 0$ and the Heisenberg approach lead to a two-sublevel scheme, the energy gaps being $2J$; however, these levels do not possess the same degeneracy in both models. In the $J' = 0$ case, the low-lying state shows a complex structure involving, simultaneously, $S = 1$ and $S = 0$ configurations.

(ii) The case $J' \neq 0$ is more interesting since it describes real compounds by taking into account the various excited configurations. It can be viewed that the fundamental is now a ninefold-degenerate state $\mid L = 1; S = 1\rangle$ corresponding to a ferromagnetic spin-spin coupling. The first excited level (sixfold degenerate) $S = 0$ is $4J'$ above the ground level. This clearly underlines the importance of the distinction between J_1 and J_2.

Further investigations of this energy scheme would not be entirely realistic when ignoring the effects of spin-orbit coupling and noncubic components of the crystal field. All these contributions can be of the same order so that we must consider the complete Hamiltonian

$$\mathcal{H} = \mathcal{H}_1 - k\lambda \sum_i \vec{L}_i \cdot \vec{S}_i$$
$$+ D \sum_i L_{iz}^2 - \beta H \sum_i (2\vec{S}_i - k\vec{L}_i) \quad (9)$$

in which all symbols have their usual meaning. The use of a fictitious orbital operator $L = 1$ results in the minus sign which affects all $\vec{L}$ components. The Stevens k parameter is an orbital reduction factor, which reflects the proportion of ligand character in the magnetic orbitals.

According to the structure of the compound under consideration we have taken the same trigonal distortion around i and j. Then, in the absence of other contributions, a positive D value will correspond to an orbital singlet ground state.
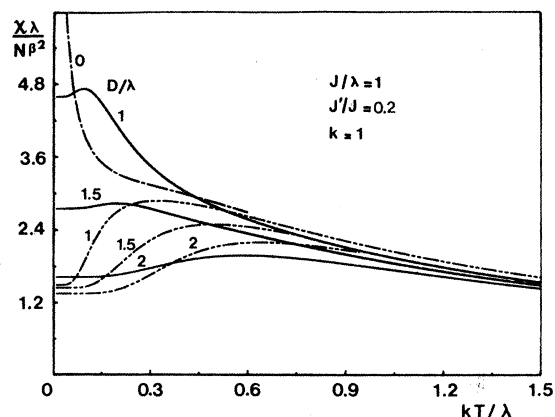
FIG. 3. Influence of the D/λ ratio on the parallel (solid line) and perpendicular (dashed line) reduced susceptibilities for constant values of the other parameters.

FIG. 5. As Fig. 3 but with negative values of the distortion parameter D/λ.

IV. THEORETICAL RESULTS AND DISCUSSION

In what follows, we have distinguished the z axis joining the two centers as being the axis of anisotropy; then the parallel $(\mathcal{X}_{\parallel})$ and perpendicular $(\mathcal{X}_{\perp})$ susceptibilities are computed from the usual expression

$$\mathcal{X}_\alpha = kT \frac{\partial^2}{\partial H_\alpha^2} \left[\ln \sum_i \exp[-E_i(H_\alpha)/kT] \right]_{H_\alpha \to 0}.$$

(10)

Furthermore, we have confined our study to positive values of λ appropriate to titanium (III).

The computational results will be discussed by reference to the graphs drawn for some selected values of both one-center (D,λ,k) and exchange (J,J') parameters (Figs. 3—7). This will allow us

to obtain useful indications concerning the role of the typical parameters before fitting the experimental data.

A. Influence of the D/λ ratio

Figure 3 corresponds to fixed values of J/λ, J'/J, and k, and D/λ scaling from 0 to 2. For $D/\lambda=0$, the susceptibility is isotropic according to the Hamiltonian (9). As kT/λ approaches zero, we notice a sharp increase of $\mathcal{X}\lambda/N\beta^2$ resulting from the fivefold-degenerate ground state with a nonzero first-order Zeeman contribution. Conversely, the magnetic behavior becomes anisotropic when the trigonal distortion of the octahedra is taken into account. This is illustrated for D/λ varying in the range 1.0—2.0. The susceptibilities exhibit a broad maximum at intermediate values of
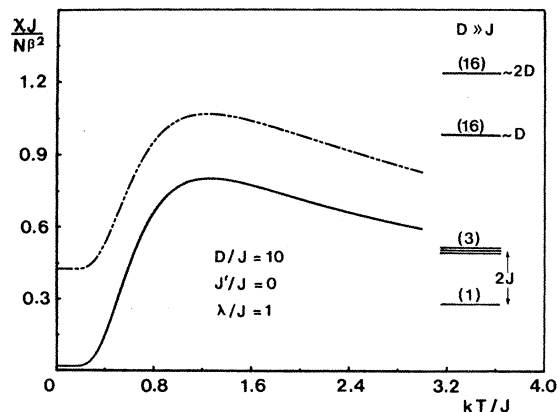

FIG. 4. Energy scheme and magnetic behavior of a binuclear unit t_{2g}^1-t_{2g}^1 with highly distorted octahedra $(D/J=10)$.
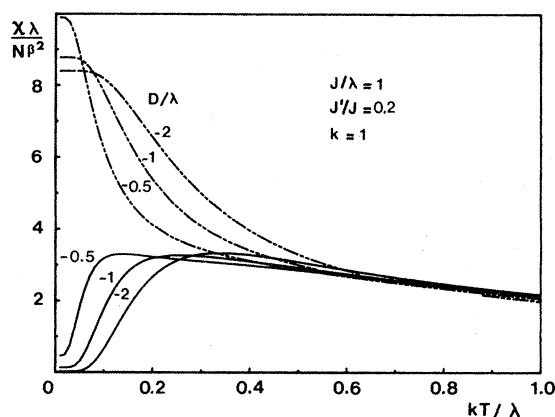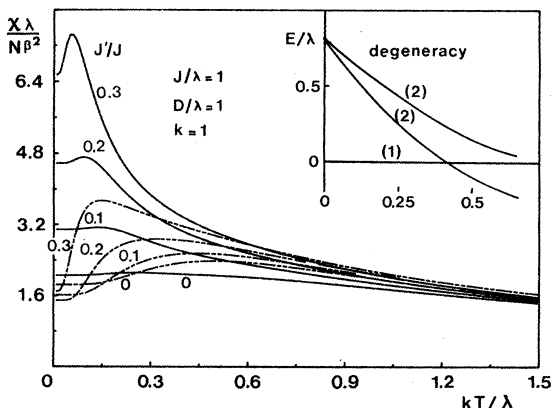

FIG. 6. Influence of the J'/J ratio on the reduced susceptibilities for constant values of the other parameters.
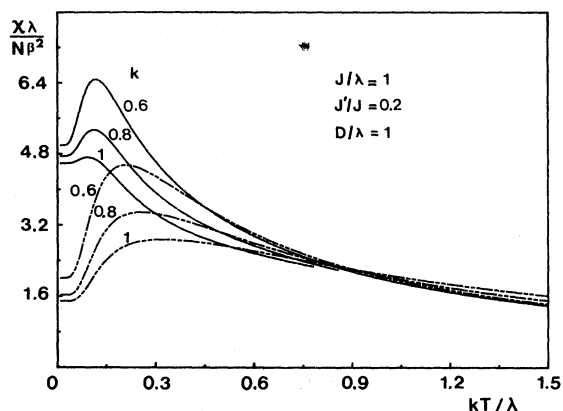
FIG. 7. Influence of the orbital reduction factor k on the reduced susceptibilities for constant values of the other parameters.

kT/λ and reach finite values in the zero-temperature limit. Such behavior results from the combined effects of the various perturbations that split the originally fivefold-degenerate level into a singlet ground state built from $|L_z, S_z\rangle = |0,0\rangle$, $|1,\bar{1}\rangle$, and $|\bar{1},1\rangle$, and two excited doublets. By mixing the fundamental to the other levels the spin-orbit coupling prevents the susceptibilities from vanishing at absolute zero.

Furthermore, in the range of examined D/λ values, we may notice that the perpendicular susceptibilities are lower than the parallel ones. Actually, the opposite situation holds for larger values (see Fig. 4), resulting from a lower weight of $|L_z = 1, S_z = -1\rangle$ and $|L_z = -1, S_z = 1\rangle$ within the ground state.

Let us now consider the case of a very large distortion parameter compared to the other ones and to the thermal energy available for the system. D is taken to be positive so that the ground term for each isolated cation is the orbital singlet A_1, well separated from the orbital doublet E. We are now dealing with a nondegenerate system with two electrons, each one in an S orbital. The remaining contributions of $\mathscr{H}$ act as perturbations and give an excited triplet at the energy $2J$ above the singlet ground state. Distinguishing the two kinds of polarized states in the exchange term changes this gap into $2(J - J')$.

Finally, for highly distorted environments, we readily verify that the eigenvalues and degeneracies of the low-lying levels are just those of the isotropic Hamiltonian

$$\mathscr{H} = 2(J - J')\vec{S}_1\vec{S}_2 .$$
(11)

The parallel component of the susceptibility may

then be expressed in a much simpler form:

$$\chi_{||} = \frac{Ng^2\beta^2}{kT}\{3 + \exp[2(J - J')/kT]\}^{-1} + \chi_{vv} ,$$
(12)

where the term χ_{vv} accounting for the second-order Zeeman contributions is due to the upper levels located around D and $2D$ (Fig. 4). Thus, it appears that the proposed model allows us to continuously describe all systems, whatever their orbital degeneracy.

Let us now consider negative D values which stabilize, contrary to the foregoing case, the E orbital doublets. The collective singlet ground state involves the states $|L_z = 0, S_z = 0\rangle$ built from the components ± 1 of L_{1z} and L_{2z} which give a zero contribution to the local moment. For decreasing values of $|D|/\lambda$, the states $|L_z = 1, S_z = -1\rangle$ and $|L_z = -1, S_z = 1\rangle$ contribute to first order in $\lambda/|D|$ to the ground state. Since they are coupled to higher levels by the magnetic momentum operator $(2\vec{S}_z - k\vec{L}_z)$, we get a weak and constant value of $\chi_{||}\lambda/N\beta^2$ in the low kT/λ limit. The first two excited levels, corresponding to linear combinations of $|L_z = 0, S_z = \pm 1\rangle$ and $|L_z = \pm 2, S_z = 0\rangle$, give rise to a large maximum of the parallel susceptibility at higher temperature. Another point of special significance concerns the susceptibility anisotropy $\chi_\perp - \chi_{||}$ which is now always positive at low temperature.

B. Influence of the exchange parameters

We first consider the J'/J ratio varying in the range $0 - 0.5$ and we assign constant values to the other parameters. It clearly appears from Fig. 6 that the J' contribution cannot be ignored without introducing a major error and we shall have to take it into account in the subsequent analysis of a real magnetic system. In order to explain the increase of the susceptibility maximum as J'/J is raised, we have to consider the low-lying levels of the system for given values of J/λ, D/λ, and k.

(i) For J'/J lower than about 0.4, the fundamental is a nondegenerate level built up from the functions $|0,0\rangle$, $|1,\bar{1}\rangle$ and $|\bar{1},1\rangle$. When J'/J approaches 0.4 the vicinity of a twofold-degenerate level containing the states $|2,0\rangle + \alpha|1,1\rangle$ and $|\bar{2},0\rangle + \alpha|\bar{1},\bar{1}\rangle$ gives rise to a sharp maximum of susceptibilities in the low-temperature range.

(ii) For J'/J greater than about 0.4, the ground state is a magnetic doublet; then the parallel com-

ponent $X_{||}\lambda/N\beta^2$ diverges as T decreases.

It would also be of interest to consider the role of J while J' remains constant. Actually, the susceptibility curves appear to be not very sensitive to the J values as may be inferred from the level diagram of Fig. 2 which shows that the splitting of the low-lying levels is J independent. This point will be of importance when determining the accuracy on the various parameters deduced from the experiment.

C. Covalency effects

In the previous discussion, the Stevens parameter k has been confined to the value $k = 1$ which corresponds to the purely ionic case. In order to illustrate the properties of the system in presence of covalency effects or configurational mixing, we now consider k values ranging from 0.6 to 1.0. This will result in modifying not only the spin-orbit coupling operator but also the expression for the magnetic moment. The main result is a sharp increase of the maximum for both parallel and perpendicular susceptibilities as k is lowered. Although this point is only of qualitative significance, since one considers an average parameter $k = k_{||} = k_\perp$ in order to simplify the discussion, this result is a clear indication of the covalency effects. In a real compound, the determination of the k factor will be based, when possible, on optical measurements; then it will be defined as being the ratio between the measured value in the compound and the free-ion value. When such measurements are not available k will be taken as an adjustable parameter.

V. MAGNETIC BEHAVIOR OF THE ISOLATED ENTITY $(Ti_2Cl_9)^{3-}$

In this section, we analyze the experimental results obtained for both parallel and perpendicular susceptibilities on $Cs_3Ti_2Cl_9$. We only refer to the model labeled I since η should be very small compared to unity. This way, the number of adjustable parameters is reduced but we must remember that a possible source of anisotropy is thus neglected.

The least-squares refinements of the experimental data have been computed for two values of the orbital reduction factor, $k = 0.8$ and $k = 0.9$, generally considered as the lower and upper limits for the Ti^{3+} ion. The best values of the various parameters and the corresponding agreement cri-

TABLE I. Results of the least-squares fitting for two values of the orbital reduction factor $k = 0.8$ and 0.9.

		$k = 0.8$	$k = 0.9$
J		549 K	520 K
J'		102 K	89 K
D		1200 K	1180 K
R	$\vec{H}||c$	3.04×10^{-2}	2.90×10^{-2}
	$\vec{H}\perp c$	2.52×10^{-2}	5.74×10^{-2}

terion, defined as the sum of the squares of the relative deviations $[\sum(X_{obs} - X_{calc})^2/X_{obs}^2]$ are reported in Table I; further, a direct comparison between experiment and predictions can be made from Fig. 8 (for $k = 0.8$). It calls for the following remarks:

(1) The agreement between theoretical and experimental values is excellent since, for $k = 0.8$, it corresponds to a mean divergence less than 2.5% on the whole temperature range. This divergence slightly increases for $k = 0.9$ but it is, perhaps, untimely to draw a conclusion on the k value. Further, it may be noticed that the fit gives a very accurate estimate of the susceptibility anisotropy.

(2) Our exchange and distortion parameters differ from those obtained in previously developed models. In particular, if we take, for comparison, $2(J - J')$ as the effective exchange parameter, it appears that this quantity is a little larger in the present study while the local distortion of the sites is significantly lower. Optical measurements in this spectral region do not allow to infer unambiguously on the accurate value of the distortion effect. Actually, we do believe that the exchange Hamiltonian cannot be of the isotropic Heisenberg form, this leading to our disagreement with previ-
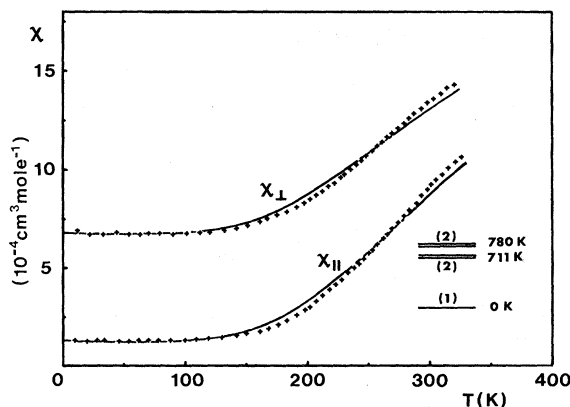

FIG. 8. Magnetic behavior of $Cs_3Ti_2Cl_9$ (from Ref. 18); comparison with the theoretical curves (solid line) obtained for $J = 549$ K, $J' = 102$ K, $D = 1200$ K, and $k = 0.8$.

ous papers. Such an approximation may only be accounted for $D \gg J$ as shown in Fig. 4.

(3) The low-lying level corresponds to a singlet ground state mainly built up from

$$\psi_0 \simeq (\mid 0,\tfrac{1}{2},0,-\tfrac{1}{2} \rangle - \mid 0,-\tfrac{1}{2},0,\tfrac{1}{2} \rangle) .$$

Then, we find two excited doublets located at 711 and 780 K with the respective structures

$$\mid L_z = \pm 1, S_z = \pm 1 \rangle$$

and

$$\mid L_z = \pm 1, S_z = 0 \rangle .$$

This energy diagram is in very good agreement with ir optical data[18] giving an energy gap close to 500 cm^{-1}($\simeq$720 K).

(4) It is worthwhile noticing that one can check the internal consistency of the values obtained for J and J' from the fit of the experimental data. Thus, the transfer integral b is related to both exchange parameters, so that it may be easily eliminated from Eq. (6), giving

$$\frac{J_1}{J_2} = \frac{U_e^a + U^s(0,0)}{U_e^a + U^s(1,0)} .$$

Further, the Coulomb repulsion between the electrons located on the same ion, U_e^a, is obtained by comparing the ionization potentials for the configurations Ti^{3+}-Ti^{3+} and Ti^{2+}-Ti^{4+}. From usual estimations[25] and taking into account the polarization effects,[13] we get $U_e^a = 1.90$ eV. The spin-spin correlation energies in the excited configurations $^3T_1$ ($S=1$) and $^1A_1,^1E,^1T_2$ ($S=0$) are determined using Racah parameters. The $^1A_1$ configuration shows an energy level which differs from the $^1E_2$ and $^1T_2$ ones. However, a convenient estimate may be obtained by weighting the corresponding values in the spin singlet states. Finally, we get $U^s(1,0) = -0.39$ eV, $U^s(0,0) = 1.17$ eV leading to the value 2.0 for the J_1/J_2 ratio, in good agreement with the experimental one 1.5. This agreement could eventually be improved if we were able to take into account accurately the reduction effects of covalency on the Coulomb integral involved in the direct calculation of J_1/J_2.

CONCLUSION

We have been able, through this work, to show that intraionic spin-spin couplings in polarized states are an essential feature for superexchange interactions. In particular, it has been shown that the exchange Hamiltonian must be expressed in a complex form including both spin and orbital components. The proposed approach which has the advantage of handling, simultaneously, various contributions, such as exchange terms, local distortions, and covalency effects, has proved to be very efficient for studying the magnetic behavior of $(Ti_2Cl_9)^{3-}$ units. We believe that the good agreement between the J_1/J_2 value deduced through the present approach and that directly calculated from ionization energies and Racah coefficients insure the quantitative quality of our approach. This should part and end to the controversies concerning the magnetic susceptibility of this compound. In the future we wish to apply such a development to other materials showing orbitally degenerate binuclear units.

ACKNOWLEDGMENT

APPENDIX

Let us introduce the exchange anisotropy for the D_{3h} configuration. The exchange Hamiltonian may be written (see text)

$$\mathscr{H}_{II} = \mathscr{H}_I + \eta \mathscr{H}' .$$

The $\mathscr{H}'$ contribution is obtained by introducing the following corrections when calculating the terms of Eq. (4):

	C_1	C_0	$C_{\bar{1}}$
C_1	$1-2\eta$	$1+\eta$	$1-2\eta$
C_0		$1+4\eta$	$1+\eta$
$C_{\bar{1}}$			$1-2\eta$

Then, $\mathscr{H}'$ is expressed as

$$\mathscr{H}' = -\tfrac{1}{2}[2L_{1z}L_{2z} - 6L_{1z}^2L_{2z}^2 + L_1^{+2}L_2^{-2} + L_1^{-2}L_2^{+2}$$

$$- (L_1^-L_{1z}L_{2z}L_2^+ + L_{1z}L_1^-L_2^+L_{2z} + L_{1z}L_1^+L_2^-L_{2z} + L_1^+L_{1z}L_{2z}L_2^-)]$$

$$\times [(J+2J') + 4J\vec{S}_1\cdot\vec{S}_2] + 4\vec{S}_1\cdot\vec{S}_2[4(J-J') - (4J-3J')(L_{1z}^2 + L_{2z}^2)] .$$

The first term stands for a pure exchange contribution while the second one mixes spin coupling with a distortionlike term $L_{1z}^2 + L_{2z}^2$.

[1]See for example: A. P. Ginsberg, Inorg. Chim. Acta Rev. 5, 45 (1971); E. Sinn, Coord. Chem. Rev. 5, 313 (1970).

[2]K. Kambe, J. Phys. Soc. Jpn. 5, 48 (1950).

[3]R. J. Elliot and M. F. Thorpe, J. Appl. Phys. 39, 802 (1968).

[4]F. Hartmann-Boutron, J. Phys. 29, 212 (1968).

[5]P. M. Levy, Phys. Rev. 177, 509 (1969).

[6]W. P. Wolf, J. Phys. C 32, 26 (1971).

[7]M. E. Lines. A. P. Ginsberg. R. L. Martin, and R. C. Sherwood, J. Chem. Phys. 57, 1 (1972).

[8]O. Kahn, Mol. Phys. 29, 1039 (1975).

[9]K. W. H. Stevens, Phys. Rep. 24, 1 (1976).

[10]P. D. N. Boyd, M. Gerloch, J. H. Harding, and R. G. Woolley, Proc. R. Soc. London Ser. A 360, 161 (1978).

[11]M. V. Eremin, V. N. Kalinenkov, and Yu. V. Rakitin, Phys. Status Solidi B 90, 123 (1978).

[12]M. Drillon and R. Georges, Phys. Rev. B 24, 1278 (1981).

[13]P. W. Anderson, Phys. Rev. 115, 2 (1959).

[14]J. B. Goodenough, Magnetism and the Chemical Bond (Wiley, New York, 1963).

[15]P. C. Crouch, G. W. A. Fowles, and R. A. Walton, J. Chem. Soc. A 1969, 972.

[16]C. G. Barraclough and A. K. Gregson, J. Chem. Soc. Faraday Trans. II 1972, 1977.

[17]R. Saillant and R. A. D. Wentworth, Inorg. Chem. 7, 1606 (1968).

[18]B. Briat, O. Kahn, I. Morgenstern Badarali, J. C. Rivoal, Inorg. Chem. 20, 4193 (1981).

[19]G. J. Wessel and J. J. W. Ijdo, Acta Cryst. 10, 466 (1957).

[20]R. Saillant and R. A. D. Wentworth, Inorg. Chem. 7, 1606 (1968).

[21]B. N. Figgis, Trans. Farad. Soc. 57, 198 (1961).

[22]F. E. Mabbs and D. J. Machin, Magnetism and Transition Metal Complexes (Chapman and Hall, London, 1973).

[23]O. Kahn and M. F. Charlot, Nouv. J. Chim. 4, 567 (1980).

[24]A. J. Freeman and R. E. Watson, Phys. Rev. 124, 1439 (1961).

[25]C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. GPO, Washington, 1952).