

Low-temperature anomalies in the magnetic and thermal properties of molecular cryocrystals doped with oxygen impurity

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Received May 17, 2000

The magnetic properties of oxygen pair clusters are investigated theoretically for different cluster geometries which can be realized by doping molecular cryomatrixes with oxygen. Anomalous temperature and pressure behavior of the magnetic susceptibility, heat capacity, and entropy is predicted. It is proposed to use these anomalies for studying the parameters characterizing the oxygen clusters and the parameters of the host matrix: the effective spin-figure interaction constant D for the molecule in the matrix, the exchange parameter J , and the number of pair clusters N_p , which can deviate markedly from the purely random value $N_p = 6Nc^2$ (N is Avogadro's number, and c is the molar concentration of the impurity). The data on the magnetic susceptibility may be used to analyze the character of the positional and orientational short-range order in the solid solution. The value of D contains information about the orientational order parameter; the distance and angular dependence of the exchange interaction parameter is still a subject of discussion in the literature. The temperature dependence of N_p contains information about diffusion and clusterization processes in the system.

PACS: 36.40.Cg, **65.40.+g**, **65.40.+m**, 75.40.Cx

1. Introduction

The study of the properties of cryocrystals doped with impurities is a well-known source of information about the impurity molecules isolated in the matrix. At the same time, rich information can be extracted from these studies on the matrix lattice dynamics and about the interaction of impurity molecules with the matrix and with each other.

Among of the most interesting in this respect are oxygen molecules, which are frequently employed as a probe of properties of atomic and molecular cryocrystals. As we know, O_2 in the electronic ground state has spin $S = 1$ and is therefore paramagnetic. The triplet ground state of O_2 , $^3\Sigma_g^-$, is split by the intermolecular spin-spin and spin-orbit interactions into a singlet with $M = 0$ and a doublet with $M = \pm 1$. The splitting for the free particle (the so-called spin-figure constant) amounts to

$D_0 = 5.71$ K [1]. Upon introduction of O_2 into a cryocrystal matrix, quasilocal levels appear in the low-energy part of the spectrum. As a result, such crystals display low-temperature anomalies in their thermal, optical, and magnetic properties.

One of the most studied is the N_2-O_2 system. Studies by Burford and Gracham [2], Sumarokov et al. [3], and Jeżowski et al. [4] were devoted to the specific heat and thermal expansion of solid nitrogen containing oxygen impurities. The anomalies found in those works correspond satisfactorily to the Schottky curve with a twofold degenerate upper level and splitting $D = 5.14$ K. The difference between D and D_0 results from the fact that the effective magnitude of the spin-figure constant for the embedded molecule in a crystal is renormalized by librational motion of the oxygen molecule [5].

With increasing concentration of the impurity, an observable number of clusters of exchange-coupled molecules appears. Their appearance affects the position and magnitude of the impurity anomalies, since the magnetic spectrum of a cluster differs from that of a single molecule [6,7].

Some further information on the impurity spectrum in N_2-O_2 solid solutions was obtained in EPR [8,9], optical [10,11], and thermal conductivity [12] studies.

There are several experimental studies of the magnetic susceptibility of cryocrystals doped with oxygen impurities [13–15], but in the absence of a theory of the magnetic properties of such solid solutions, little information was extracted from these studies. At the same time, magnetic systems containing magnetically active molecules or molecular groups can exhibit unusual magnetic properties [16,17] as compared with ordinary magnets. In addition to solid oxygen and oxygen-containing solid solution of cryocrystals, some alkali hyperoxides are examples of such magnetic systems. The magnetic Hamiltonian in this case contains a new parameter, the angle θ between molecular axes. For matrix-embedded oxygen clusters this parameter is matrix-dependent. For example, in the case of a fluorine matrix, the angle θ is close to zero (the collinear cluster), for an α -nitrogen matrix, $\theta \approx \arccos(1/3)$, and for a γ -nitrogen matrix, $\theta \approx \pi/2$ (the orthogonal cluster).

In comparison with heat capacity studies, the magnetic measurements can be performed in high-pressure conditions, which makes it possible to use oxygen molecules as a probe for cryocrystals under high-pressure conditions.

In this paper we obtained exact analytical expressions for the contribution of a pair oxygen cluster to the magnetic susceptibility as a function of the parameters of the magnetic Hamiltonian — the intermolecular exchange interaction constant, the spin-figure constant, and the angle θ between the molecular axes. It will be shown that the magnetic susceptibility is very sensitive to changes in these parameters, and it is this sensitivity that makes the magnetic susceptibility an additional convenient characteristic for studying properties of both the host matrix and oxygen clusters. The most peculiar anomalies in the behavior of the magnetic heat capacity and magnetic entropy will be discussed in brief.

2. General equations

The spin Hamiltonian of an exchange-coupled pair of oxygen molecules can be written as [3,7]

$$\mathcal{H} = \mathcal{H}_{sf} + \mathcal{H}_{ex} ; \quad (2.1)$$

$$\mathcal{H}_{sf} = D[(\mathbf{S}_1 \mathbf{n}_1)^2 + (\mathbf{S}_2 \mathbf{n}_2)^2 - \frac{2}{3} S(S+1)] , \quad (2.2)$$

$$\mathcal{H}_{ex} = J \mathbf{S}_1 \mathbf{S}_2 , \quad (2.3)$$

where D is the spin-figure constant, \mathbf{S}_i are spin operators ($S = 1$), \mathbf{n}_i are the unit vectors of the molecular axes, and J is the exchange interaction constant.

In a magnetic field $\mathbf{H} = H\mathbf{j}$, where \mathbf{j} is the unit vector along the magnetic field, the Hamiltonian (2.1) acquires an additional term, the Zeeman energy

$$\mathcal{H}_Z = -\mu_B g \mathbf{H}(\mathbf{S}_1 + \mathbf{S}_2) , \quad (2.4)$$

where μ_B is the Bohr magneton and g is the splitting factor.

An exact analytical expression for the zero-field magnetic susceptibility for the system described by the Hamiltonian (2.1) can be obtained by using perturbation theory, with Eq. (2.1) as the unperturbed Hamiltonian and the Zeeman interaction term (2.4) as the perturbation [18]. The total Hamiltonian for the system in the magnetic field is

$$\mathcal{H}_{tot} = \mathcal{H}_{sf} + \mathcal{H}_{ex} + \mathcal{H}_Z . \quad (2.5)$$

Let $E_i = E_i(H)$ be the set of eigenvalues of \mathcal{H}_{tot} . Then the free energy \mathcal{F} , the magnetic moment M , and the magnetic susceptibility χ are given by the equations

$$\mathcal{F} = -T \ln \sum_i e^{-\beta E_i(H)} ; \quad (2.6)$$

$$M = \frac{\partial \mathcal{F}}{\partial H} = -\frac{1}{Z} \sum_i \frac{\partial E_i}{\partial H} e^{-\beta E_i(H)} \quad (2.7)$$

$$\chi = \frac{\partial M}{\partial H} = -\frac{1}{Z} \sum_i \frac{\partial^2 E_i}{\partial H^2} e^{-\beta E_i(H)} + \frac{\beta}{Z} \sum_i \left(\frac{\partial E_i}{\partial H} \right)^2 e^{-\beta E_i(H)} - \frac{\beta}{Z^2} \left[\sum_i \frac{\partial E_i}{\partial H} e^{-\beta E_i(H)} \right]^2 , \quad (2.8)$$

where $\beta = 1/T$, $Z = \sum_i \exp(-E_i/T)$.

The energy corrections to the eigenvalues of the unperturbed Hamiltonian can be written in the form of a series in the magnetic field:

$$E_i(H) = E_i^{(0)} + \sum_{k=1}^{\infty} (\mu_B g)^k a_{ik} H^k. \quad (2.9)$$

Taking into account the relations

$$\frac{\partial E_i}{\partial H} = \sum_{k=1}^{\infty} (\mu_B g)^k a_{ik} k H^{k-1}; \quad (2.10)$$

$$\frac{\partial^2 E_i}{\partial H^2} = \sum_{k=1}^{\infty} (\mu_B g)^k a_{ik} k(k-1) H^{k-2},$$

we get the final expression for the zero-field magnetic susceptibility

$$\chi(T)_{H=0} = (\mu_B g)^2 \left\{ \frac{\langle a_{i1}^2 \rangle}{T} - 2\langle a_{i2} \rangle \right\}, \quad (2.11)$$

where

$$\langle a_{i1}^2 \rangle = \frac{1}{Z} \sum_i a_{i1}^2 \exp(-E_i/T); \quad (2.12)$$

$$\langle a_{i2} \rangle = \frac{1}{Z} \sum_i a_{i2} \exp(-E_i/T);$$

The last term in Eq. (2.8), which is the squared magnetic moment, vanishes in the limit of zero magnetic field (there is no spontaneous magnetization in the system under consideration), i.e., the following equality holds:

$$\sum_i a_{i1} e^{-\beta E_i^0} = 0. \quad (2.13)$$

Thus the zero-field magnetic susceptibility is defined by the eigenvalues $E_i^{(0)}$ and by the coefficients a_{i1} and a_{i2} which determine first- and second-order corrections in the perturbation theory.

The eigenvalues $E_i^{(0)}$ determine the magnetic part of the impurity contribution to the heat capacity and entropy. The magnetic heat capacity is given by the expression

$$\frac{C_m}{k_B} = \frac{1}{T^2} \{ \langle E^2 \rangle - \langle E \rangle^2 \}, \quad (2.14)$$

where

$$\langle E^2 \rangle = \frac{1}{Z} \sum_i E_i^2 \exp(-E_i/T); \quad (2.15)$$

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i \exp(-E_i/T).$$

In a similar way, the magnetic entropy is given by the expression

$$\frac{S_m}{k_B} = \ln Z + \frac{\langle E \rangle}{T}. \quad (2.16)$$

Thus, Eqs. (2.11), (2.14), and (2.16) give the contribution of the discrete set of magnetic energy levels to the magnetic susceptibility, magnetic heat capacity, and magnetic entropy, respectively.

3. Spectrum of exchange-coupled O_2-O_2 pair in zero magnetic field

In order to calculate the coefficients a_{i1} and a_{i2} one needs to have a complete set of eigenvectors and eigenvalues of the unperturbed Hamiltonian (2.1).

The symmetry group of the Hamiltonian (2.1) is D_{2h} [7], that is, the system under consideration has three mutually perpendicular twofold symmetry axis. Let us transform the coordinate system in such a way that allow us to use the symmetry considerations explicitly. First of all, we execute a parallel translation, making the centers of mass of the molecules coincide. This transformation does not change the symmetry of the Hamiltonian (2.1) and thus does not change the spectrum of the system. Then it

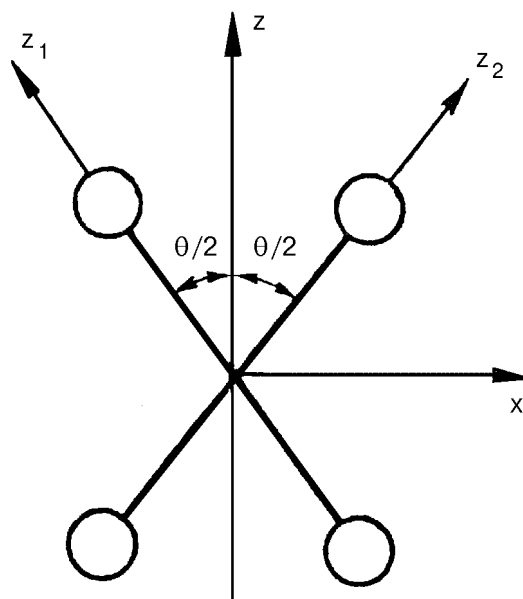


Fig. 1. Coordinate systems related to the molecular axes.

is natural to choose the coordinate system x, y, z with the molecules lying in the xz plane and with the z axis directed along the bisectrix of the angle between the molecular axes.

Let us introduce two intrinsic coordinate systems (x_1, y_1, z_1) and (x_2, y_2, z_2) with the local z axis rotated with respect to the z axis by the angle $\pm \theta/2$ in the xz plane, so the local z_i axis is directed along the axis of the i th molecule (Fig. 1). The relation between the components of the spin operators in the fixed and rotated coordinate systems are:

$$\begin{aligned} S_{1x} &= S_{1x_1} \cos \frac{\theta}{2} + S_{1z_1} \sin \frac{\theta}{2}; \\ S_{1y} &= S_{1y_1}; \\ S_{1z} &= -S_{1x_1} \sin \frac{\theta}{2} + S_{1z_1} \cos \frac{\theta}{2}; \\ S_{2x} &= S_{2x_2} \cos \frac{\theta}{2} - S_{2z_2} \sin \frac{\theta}{2}; \\ S_{2y} &= S_{2y_2}; \\ S_{2z} &= S_{2x_2} \sin \frac{\theta}{2} + S_{2z_2} \cos \frac{\theta}{2}. \end{aligned} \quad (3.1)$$

Replacing the Cartesian spin components defined in the intrinsic coordinate systems by cyclic spin components according to the relations:

$$\begin{aligned} S_{1x_1} &= \frac{1}{\sqrt{2}} (S_1^- - S_1^+); \quad S_{2x_2} = \frac{1}{\sqrt{2}} (S_2^- - S_2^+); \\ S_{1y_1} &= \frac{i}{\sqrt{2}} (S_1^- + S_1^+); \quad S_{2y_2} = \frac{i}{\sqrt{2}} (S_2^- + S_2^+); \end{aligned} \quad (3.2)$$

we transform the Hamiltonian (2.1) into the form

$$\begin{aligned} \mathcal{H} &= D \left[S_{1z_1}^2 + S_{2z_2}^2 - \frac{2}{3} S(S+1) \right] + J \left\{ S_{1z_1} S_{2z_2} \cos \theta - \right. \\ &- (S_1^- S_2^+ + S_1^+ S_2^-) \cos^2 \frac{\theta}{2} - (S_1^- S_2^- + S_1^+ S_2^+) \sin^2 \frac{\theta}{2} + \\ &\left. + \frac{1}{\sqrt{2}} \left[(S_2^- - S_2^+) S_{1z_1} - (S_1^- - S_1^+) S_{2z_2} \right] \sin \theta \right\}. \end{aligned} \quad (3.3)$$

From the nine states $|S_{1z_1}\rangle |S_{2z_2}\rangle$ of the O_2 - O_2 pair ($S_{1z_1}, S_{2z_2} = 0, \pm 1$) that realize the reproducible representation

$$\Gamma = 4A_{1g} + 2B_{1g} + B_{2g} + 2B_{3g}, \quad (3.4)$$

we can form 9 orthonormal basis functions Φ_i that transform according to the four irreducible representations of the group D_{2h} (see Appendix A).

Because of the symmetry, the matrix elements of the Hamiltonian (3.3) between states Φ_i that transform according to different irreducible representations are zero. As a result, the Hamiltonian matrix in the basis of the functions Φ_i assumes the block-diagonal form

$$\mathcal{H} = \begin{pmatrix} \mathcal{H}_{B_{2g}} & 0 & 0 & 0 \\ 0 & \mathcal{H}_{B_{1g}} & 0 & 0 \\ 0 & 0 & \mathcal{H}_{B_{3g}} & 0 \\ 0 & 0 & 0 & \mathcal{H}_{A_{1g}} \end{pmatrix}, \quad (3.5)$$

where

$$\begin{aligned} \mathcal{H}_{B_{2g}} &= D + J; \\ \mathcal{H}_{B_{1g}} &= \begin{pmatrix} D - J \cos \theta & -J \sin \theta \\ -J \sin \theta & 2D + J \cos \theta \end{pmatrix}; \\ \mathcal{H}_{B_{3g}} &= \begin{pmatrix} D + J \cos \theta & J \sin \theta \\ J \sin \theta & 2D - J \cos \theta \end{pmatrix}; \\ \mathcal{H}_{A_{1g}} &= \begin{pmatrix} 0 & -J & J \cos \theta & 0 \\ -J & 2D & J \cos \theta & 0 \\ J \cos \theta & J \cos \theta & 2D & -\sqrt{2}J \sin \theta \\ 0 & 0 & -\sqrt{2}J \sin \theta & D - J \end{pmatrix}. \end{aligned} \quad (3.6)$$

The constant term $(2/3)DS(S+1)$, which determines the reference level for the spectrum, was omitted in transforming the Hamiltonian (3.3) into the form Eq. (3.6).

For two interesting cases, $\theta = 0$ (the collinear cluster) and $\theta = \pi/2$ (the orthogonal cluster), all the unperturbed eigenvectors and eigenvalues can be found in an explicit analytical form, which in turn permits finding analytical expressions for the zero-field magnetic susceptibility. In the general case, analytical expressions can be found for the eigenvectors and eigenvalues corresponding to representations B_{1g} , B_{2g} , and B_{3g} , and the rest can be found by numerical diagonalization of the Hamiltonian $\mathcal{H}_{A_{1g}}$ (Eq. (3.6)). The eigenvectors and eigenvalues are given in Appendix B.

The spectrum of an exchange-coupled pair of oxygen molecules as a function of the parameter J/D for different angles between the molecular

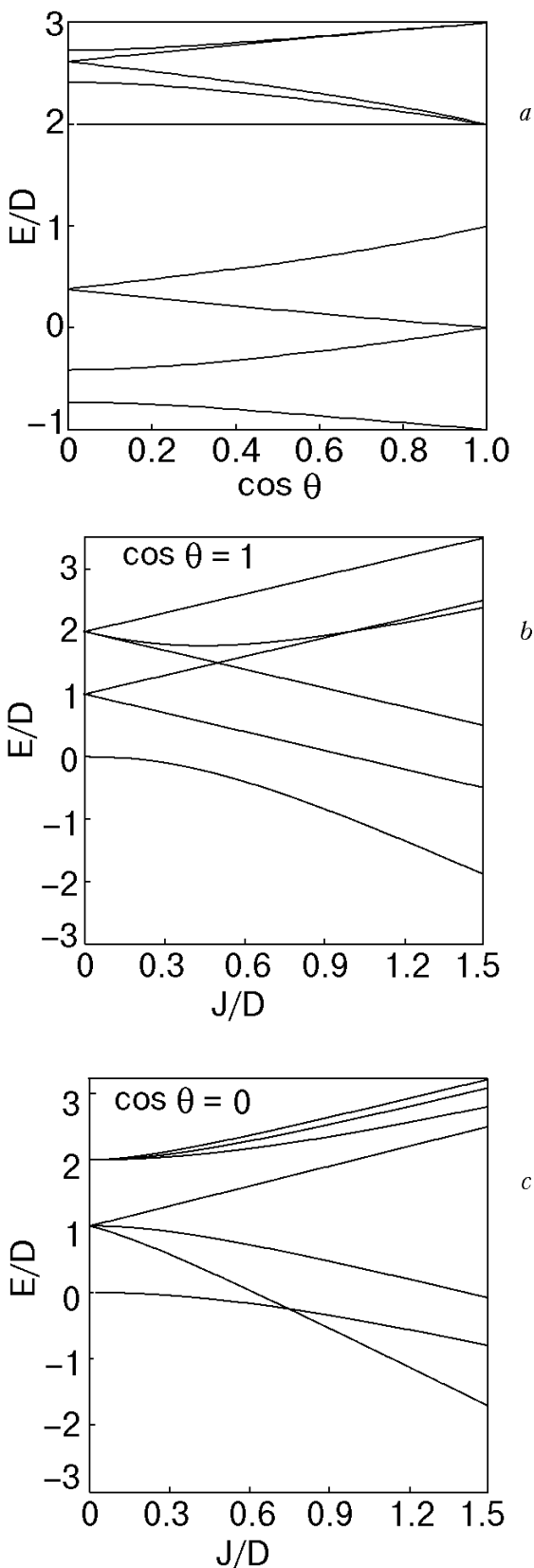


Fig. 2. Energy spectra of exchange-coupled pair oxygen clusters. Dependence of the energy spectrum on: the angle between the axes of the molecules ($J/D = 1$) (a); J/D for the collinear cluster (b) and for the orthogonal cluster (c).

axes is shown in Fig. 2. Figure 2,a illustrates the sensitivity of the spectrum to the parameter θ . Figures 2,b,c give the spectrum as a function of J/D for the collinear and orthogonal cluster, respectively. In the region $J/D \ll 1$ for all angles θ , the spectrum of the cluster is close to the spectrum of noninteracting molecules, and the effect of the exchange interaction is small. In the opposite limiting case $J/D \gg 1$ the behavior of the spectrum is also in fact universal for all angles. In the limit $J/D \rightarrow \infty$ the nine levels of the (${}^3\Sigma_g^-$) (${}^3\Sigma_g^-$) ground state of the pair split into a quintet of energy $+J$ (states with the total spin of the pair $S = 2$), a triplet of energy $-J$ (total spin of the pair $S = 1$), and a singlet of energy $-2J$ (total spin of the pair $S = 0$). In the region $J/D \sim 1$ the spectrum of the cluster depends essentially on the angle between the molecular axes.

At low temperatures the thermal properties of the system (the heat capacity and the thermal expansion) are determined primarily by the gap between the ground state and the first excited state of the system ΔE . This value depends essentially on both J/D and θ . Near $\theta = \pi/2$ there is a certain range of θ where the two lowest levels as a function of J/D intersect. At $\theta = \pi/2$ the intersection takes place at $J/D = 3/4$ (Fig. 2,c).

It is this sensitivity of the low-temperature thermal properties of the system to the position and to the value of the energy gap ΔE as a function of J/D and θ that was used in Refs. 3,7 to obtain information about the dependence of the exchange interaction of oxygen molecules on both the intermolecular separation and the intermolecular orientations.

As will be shown below, the zero-field magnetic susceptibility is strongly J/D and θ dependent; as a result, the low-temperature zero-field magnetic susceptibility can be used as a source of information on the peculiarities of the O_2-O_2 exchange interaction.

4. Zero-field magnetic susceptibility

4.1. Collinear O_2-O_2 cluster ($\theta = 0$)

Transverse susceptibility ($\chi_{xx} = \chi_{yy}$). The spin spectrum of a collinear O_2-O_2 cluster consists in general of three doublet levels and three singlets. In the limit $J/D = 0$ corresponding to a pair of noninteracting molecules, the nine levels of the system are split into the ground-state singlet and two quadruplets; in the opposite limit $J/D = \infty$ the spectrum consists of a singlet, a triplet, and a quintet (Fig. 2,a). An additional degeneracy occurs

at $J/D = 1/2$ and $J/D = 1$. All these particular cases should be considered separately.

It is easy to check that all the energy corrections of the first order are zero:

$$\Delta E_i^{(1)} = \langle \Psi_i | \mathcal{H}_Z | \Psi_i \rangle = 0. \quad (4.1)$$

The energy corrections of the second order can be found from the equation

$$\Delta E_i^{(2)} = \sum_{k \neq i} \frac{|\langle \Psi_i | \mathcal{H}_Z | \Psi_k \rangle|^2}{E_i^{(0)} - E_k^{(0)}} \quad (4.2)$$

in the case of nondegenerate levels; in the case of doublet levels the energy corrections can be found from the secular equation

$$\begin{vmatrix} \sum_{l \neq m} \frac{\mathcal{H}_Z^{ml} \mathcal{H}_Z^{lm}}{E_m^{(0)} - E_l^{(0)}} - \Delta E^{(2)} & \mathcal{H}_Z^{mn} + \sum_{l \neq m} \frac{\mathcal{H}_Z^{ml} \mathcal{H}_Z^{ln}}{E_m^{(0)} - E_l^{(0)}} \\ \mathcal{H}_Z^{nm} + \sum_{l \neq n} \frac{\mathcal{H}_Z^{nl} \mathcal{H}_Z^{lm}}{E_n^{(0)} - E_l^{(0)}} & \sum_{l \neq n} \frac{\mathcal{H}_Z^{nl} \mathcal{H}_Z^{ln}}{E_n^{(0)} - E_l^{(0)}} - \Delta E^{(2)} \end{vmatrix} = 0, \quad (4.3)$$

where Ψ_i and $E_i^{(0)}$ are listed in Appendix B.

As follows from Eq. (4.1),

$$a_i^{(1)} = 0, \quad i = 1, 2, \dots, 9. \quad (4.4)$$

After finding the matrix elements with the help of Ψ_i given in Appendix B, we get from Eqs. (4.2) and (4.3) the set of coefficients $a_i^{(2)}$:

$$\begin{aligned} a_1^{(2)} &= a_9^{(2)} = -\frac{1}{D}; \quad a_2^{(2)} = 0; \\ a_3^{(2)} &= a_5^{(2)} = a_6^{(2)} = \frac{1}{D}; \\ a_7^{(2)} &= \frac{2}{D} \frac{(J + \frac{1}{2} E_7^{(0)})^2}{J^2 + \frac{1}{2} (E_7^{(0)})^2} \left[\left(1 - \frac{J}{D} + \frac{9}{4} \frac{J^2}{D^2} \right)^{1/2} - \frac{3}{2} \frac{J}{D} \right]^{-1}; \\ a_8^{(2)} &= -\frac{2}{D} \frac{(J + \frac{1}{2} E_8^{(0)})^2}{J^2 + \frac{1}{2} (E_8^{(0)})^2} \left[\left(1 - \frac{J}{D} + \frac{9}{4} \frac{J^2}{D^2} \right)^{1/2} + \frac{3}{2} \frac{J}{D} \right]^{-1}; \\ a_4^{(2)} &= -\frac{1}{D} - \left(a_7^{(2)} + a_8^{(2)} \right). \end{aligned} \quad (4.5)$$

A sum rule holds for the coefficients $a_i^{(2)}$:

$$\sum_i a_i^{(2)} = 0. \quad (4.6)$$

Taking into account that all the $a_i^{(1)}$ coefficients equal zero (Eq. (4.4)), the transverse zero-field magnetic susceptibility for a collinear cluster is described by the expression

$$\chi_{\perp} = -2(\mu_B g)^2 \frac{\sum_i a_i^{(2)} e^{-\beta E_i^{(0)}}}{\sum_i e^{-\beta E_i^{(0)}}}. \quad (4.7)$$

Let us consider now the limiting cases $J/D \rightarrow 0$ and $J/D \rightarrow \infty$. Generally speaking, since the spectrum for each of these cases has a structure that differs from that considered above, each of them should be treated separately. In fact, the result may be obtained from the same Eq. (4.7) if we find the corresponding limits. Really, the only condition to be met is the condition of applicability of the perturbation theory, i.e., the separation between levels, which we consider as belonging to different zero-order energies, should be large compared with the perturbation energy. In the case $J/D \rightarrow 0$ the separation between the levels which tend to form quadruplets goes to zero as J , so the following inequality should hold:

$$J \gg \mu_B g H. \quad (4.8)$$

Thus, in passing to the limits $J/D \rightarrow 0$, $H \rightarrow 0$ in Eq. (4.7), we must take them in such a way that the inequality (4.8) is obeyed.

When $J/D \rightarrow 0$, $D \neq 0$ the limiting values of the $a_i^{(2)}$ and $E_i^{(0)}$ are as follows:

$$\begin{aligned} a_8^{(2)} &= -\frac{2}{D}, \quad E_8^{(0)} = 0; \quad a_1^{(2)} = a_9^{(2)} = -\frac{1}{D}; \\ a_2^{(2)} &= a_4^{(2)} = 0; \quad E_1^{(0)} = E_2^{(0)} = E_4^{(0)} = E_9^{(0)} = D; \\ a_3^{(2)} &= a_5^{(2)} = a_6^{(2)} = a_7^{(2)} = \frac{1}{D}; \\ E_3^{(0)} &= E_5^{(0)} = E_6^{(0)} = E_7^{(0)} = 2D. \end{aligned} \quad (4.9)$$

As a result, we get

$$\chi_{\perp} = 4(\mu_B g)^2 \frac{1}{D} \frac{1 - e^{-\beta D}}{1 + 2e^{-\beta D}}, \quad (4.10)$$

which is twice the transverse susceptibility for a molecule described by the Hamiltonian $\mathcal{H} = DS_z^2$.

When $D \rightarrow 0$, $J \neq 0$,

$$a_7^{(2)} = -\frac{9}{D}, \quad E_7^{(0)} = J + \frac{2}{3}D;$$

$$a_8^{(2)} = 0, \quad E_8^{(0)} = -2J. \quad (4.11)$$

As a result, we get

$$\chi_{\perp} = 2(\mu_B g)^2 \frac{1}{T} e^{-\beta J} \frac{1 + 5 e^{-2\beta J}}{1 + 3 e^{-\beta J} + 5e^{-3\beta J}}, \quad (4.12)$$

the magnetic susceptibility of a Heisenberg antiferromagnet pair cluster.

In the low-temperature limit $\beta\Delta E \gg 1$, where ΔE is the gap between the ground and the first excited levels, taking into account only the two lowest levels, we get

$$\begin{aligned} \chi_{\perp}(T \rightarrow 0) &= \\ &= 2(\mu_B g)^2 |a_8^{(2)}| \left\{ 1 + \left(\frac{1}{D|a_8^{(2)}|} - 2 \right) \exp\left(-\frac{\Delta E}{T}\right) \right\}, \\ \Delta &= \left(D^2 - DJ + \frac{9}{4}J^2 \right)^{1/2} - \frac{J}{2}, \end{aligned} \quad (4.13)$$

where $a_8^{(2)}$ is defined by Eq. (4.5).

The zero-temperature limit

$$\begin{aligned} \chi_{\perp}(T = 0) &= \\ &= 4(\mu_B g)^2 \frac{(J + \frac{1}{2} E_8^{(0)})^2}{J^2 + \frac{1}{2} (E_8^{(0)})^2} \left[\left(D^2 - DJ + \frac{9}{4}J^2 \right)^{1/2} + \frac{3}{2} \frac{J}{D} \right]^{-1}, \end{aligned} \quad (4.14)$$

where the ground state energy

$$E_8 = +D - \frac{1}{2}J - (D^2 - DJ + \frac{9}{4}J^2)^{1/2}. \quad (4.15)$$

In the limiting case of small and large J/D we get

$$\chi_{\perp}(T = 0) = (\mu_B g)^2 \frac{4}{D} \begin{cases} \left(1 - 2 \frac{J}{D} \right), & \frac{J}{D} \ll 1 \\ \frac{4}{81} \left(\frac{D}{J} \right)^3, & \frac{J}{D} \gg 1. \end{cases} \quad (4.16)$$

Thus, at small J/D , the zero-temperature transverse susceptibility decreases linearly with rising J/D , but at large J this quantity is practically suppressed.

In the high-temperature limit $\beta\Delta E \gg 1$, expanding Eq. (4.7) in powers of inverse temperature, we get corrections to Curie law:

$$\begin{aligned} \chi_{\perp} &= \frac{4}{3} (\mu_B g)^2 \frac{1}{T} \times \\ &\times \left\{ 1 + \left(\frac{1}{6}D - \frac{2}{3}J \right) \frac{1}{T} - \left(\frac{1}{18}D^2 + \frac{2}{9}DJ + \frac{1}{6}J^2 \right) \frac{1}{T^2} + \dots \right\}. \end{aligned} \quad (4.17)$$

The expression in curly brackets gives the corrections to the Curie law.

Longitudinal susceptibility. As in the case of the transverse susceptibility, the coefficients $a_i^{(1)}$ and $a_i^{(2)}$ can be found from the first- and second-order energy corrections. As a result, we arrive at the following sets of coefficients $a_i^{(1)}$ and $a_i^{(2)}$:

$$\begin{aligned} a_1^{(1)} = a_2^{(1)} = 1; \quad a_3^{(1)} = 2; \quad a_4^{(1)} = a_9^{(1)} = -1; \\ a_6^{(1)} = -2; \quad a_5^{(1)} = a_7^{(1)} = a_8^{(1)} = 0. \end{aligned} \quad (4.18)$$

All the coefficients $a_i^{(2)}$ vanish in this case:

$$a_i^{(2)} = 0, \quad i = 1, \dots, 9. \quad (4.19)$$

Substituting the coefficients $a_i^{(1)}$ from Eq. (4.18) into Eq. (2.11) and taking into account Eq. (4.19), we arrive at the following expression for the longitudinal susceptibility:

$$\chi_{\parallel} = \chi_{zz} = \frac{2(\mu_B g)^2 e^{-\beta(D-J)} + e^{-\beta(D+J)} + 4e^{-\beta(2D+J)}}{T \sum_i e^{-\beta E_i}}. \quad (4.20)$$

Considering that in this case the perturbation operator Eq. (2.4) commutes with the spin-figure interaction Hamiltonian \mathcal{H}_{sf} , the result (Eq. (4.20)) can be readily obtained by employing the fluctuation-dissipation relation [19]

$$\chi_{zz} = \frac{(\mu_B g)^2 \text{Sp} (S_{1z}^2 + S_{2z}^2) e^{-\beta\mathcal{H}}}{T \text{Sp} e^{-\beta\mathcal{H}}}. \quad (4.21)$$

At low temperatures the longitudinal susceptibility exponentially goes to zero:

$$\chi_{zz} = 2 \frac{(\mu_B g)^2}{T} \exp\left[-\frac{1}{T} \left(D^2 - DJ + \frac{9}{4}J^2 \right)^{1/2} - \frac{J}{2}\right]. \quad (4.22)$$

The high-temperature expansion has the form

$$\chi_{zz} = \frac{4}{3} (\mu_B g)^2 \frac{1}{T} \left\{ 1 - \left(\frac{1}{3} D + \frac{2}{3} J \right) \frac{1}{T} + \left(-\frac{1}{18} D^2 + \frac{4}{9} D J - \frac{1}{6} J^2 \right) \frac{1}{T^2} + \dots \right\}. \quad (4.23)$$

At $J = 0$ Eq. (4.20) reduces to

$$\chi_{zz} = 4(\mu_B g)^2 \frac{1}{T} \frac{e^{-\beta D}}{1 + 2e^{-\beta D}}, \quad (4.24)$$

which is the longitudinal susceptibility for two noninteracting molecules.

At $D = 0$, Eq. (4.20) reduces to Eq. (4.12), the magnetic susceptibility of a Heisenberg antiferromagnetic cluster.

Average susceptibility. The average or powder susceptibility is given by the expression

$$\bar{\chi} = \frac{1}{3} \chi_{\parallel} + \frac{2}{3} \chi_{\perp}. \quad (4.25)$$

In the general case $\bar{\chi}$ is given by Eqs. (4.4), (4.5), (4.7), and (4.20).

The low-temperature asymptotic expression for $\bar{\chi}$ is

$$\bar{\chi}(T \rightarrow 0) = \frac{2}{3} (\mu_B g)^2 \times \left\{ 2|a_8^{(2)}| + \left[\frac{1}{T} + 2|a_8^{(2)}| \left(\frac{1}{D|a_8^{(2)}|} - 2 \right) \right] \exp \left(-\frac{\Delta}{T} \right) \right\}, \quad (4.26)$$

where $a_8^{(2)}$ is defined by Eq. (4.5) and Δ , the gap between the ground and the first excited levels, is given by Eq. (4.13).

At zero temperature in the limiting case of small and large J/D we get

$$\bar{\chi}(T = 0) = \frac{8}{3} (\mu_B g)^2 \frac{1}{D} \begin{cases} \left(1 - 2 \frac{J}{D} \right), & \frac{J}{D} \ll 1 \\ \frac{4}{81} \left(\frac{D}{J} \right)^3, & \frac{J}{D} \gg 1. \end{cases} \quad (4.27)$$

The high-temperature asymptotic expression for $\bar{\chi}$ is given by Eqs. (4.17) and (4.23):

$$\bar{\chi} = \frac{4}{3} (\mu_B g)^2 \frac{1}{T} \left\{ 1 - \frac{J}{T} - \frac{1}{18} \frac{D^2 + 3J^2}{T^2} + \dots \right\}. \quad (4.28)$$

As one can see, the factor that determines the deviation of the average susceptibility from the Curie law at high temperatures contains no terms linear in the spin-figure constant D , at any rate in terms up to T^{-2} .

4.2. Orthogonal O_2 - O_2 cluster ($\theta = \pi/2$)

The eigenfunctions and eigenvalues of the unperturbed Hamiltonian (3.5) can be found readily in this case in analytical form (see Appendix B). In order of decreasing energy, the sequence of terms is as follows:

$$E_8 \geq E_3 = E_5 \geq E_6 > E_1 > E_2 = E_4 \geq E_7, E_9. \quad (4.29)$$

There are two doublets; for the others the equality sign, where indicated is realized for the limiting cases $D = 0$ and $J = 0$. The only crossing occurs between the E_7 and E_9 levels at $J/D = 3/4$ (Fig. 2,c). At $J/D > 3/4$ the ground level is the E_9 term, and otherwise it is the E_7 term.

Calculation of the $\chi_{xx} = \chi_{zz}$ components. In the general case ($\theta \neq 0$), classification of the components into transverse and longitudinal loses meaning, but in the case $\theta = \pi/2$ the equality $\chi_{xx} = \chi_{zz}$ holds from symmetry considerations, so these components, can be considered as an analog of the transverse component, while χ_{yy} is an analog of the longitudinal component.

Let us consider first the general case of J/D ; the special case $J/D = 3/4$ will be considered below. We will proceed in the same manner as in the previous Section. As a result, we get the following sets of coefficients $a_i^{(1)}$ and $a_i^{(2)}$:

$$a_i^{(1)} = 0, \quad i = 1, 2, \dots, 9;$$

$$a_1^{(2)} = -(a_2^{(2)} + a_3^{(2)}); \quad a_2^{(2)} = -\frac{1}{2} \frac{(m_2 - l_2)^2}{J \pm \left(\frac{1}{4} D^2 + J^2 \right)^{1/2} - \frac{D}{2}};$$

$$\begin{aligned}
a_4^{(2)} &= \frac{(l_4 l_6 - m_4 m_6)^2}{\frac{D}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} - (D^2 + J^2)^{1/2}} + \frac{(l_4 l_7 - m_4 m_7)^2}{\frac{D}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} + (D^2 + J^2)^{1/2}} + (l_4 + m_4)^2 \times \\
&\times \left\{ \frac{(l_8 - m_8/\sqrt{2})^2}{\left[\frac{J}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} - \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2\right)^{1/2}\right]} + \frac{(l_9 - m_9/\sqrt{2})^2}{\left[\frac{J}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} + \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2\right)^{1/2}\right]} \right\}; \\
a_5^{(2)} &= \frac{(l_5 l_6 - m_5 m_6)^2}{\frac{D}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} - (D^2 + J^2)^{1/2}} + \frac{(l_5 l_7 - m_5 m_7)^2}{\frac{D}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} + (D^2 + J^2)^{1/2}} + (l_5 + m_5)^2 \times \\
&\times \left\{ \frac{(l_8 - m_8/\sqrt{2})^2}{\left[\frac{J}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} - \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2\right)^{1/2}\right]} + \frac{(l_9 - m_9/\sqrt{2})^2}{\left[\frac{J}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} + \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2\right)^{1/2}\right]} \right\}; \\
a_6^{(2)} &= - \left\{ \frac{(l_4 l_6 - m_4 m_6)^2}{\left[\frac{D}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} - (D^2 + J^2)^{1/2}\right]} + \frac{(l_5 l_6 - m_5 m_6)^2}{\left[\frac{D}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} - (D^2 + J^2)^{1/2}\right]} \right\}; \\
a_7^{(2)} &= - \left\{ \frac{(l_4 l_7 - m_4 m_7)^2}{\left[\frac{D}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} + (D^2 + J^2)^{1/2}\right]} + \frac{(l_5 l_7 - m_5 m_7)^2}{\left[\frac{D}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} + (D^2 + J^2)^{1/2}\right]} \right\}; \\
a_8^{(2)} &= - \left(l_8 - \frac{1}{\sqrt{2}} m_8 \right)^2 \times \\
&\times \left\{ \frac{(l_4 + m_4)^2}{\left[\frac{J}{2} - \left(\frac{1}{4} D^2 + J^2\right)^{1/2} \mp \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2\right)^{1/2}\right]} + \frac{(l_5 + m_5)^2}{\left[\frac{J}{2} + \left(\frac{1}{4} D^2 + J^2\right)^{1/2} \mp \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2\right)^{1/2}\right]} \right\}.
\end{aligned} \tag{4.30}$$

The magnetic susceptibility $\chi_{xx} = \chi_{zz}$ is defined by Eq. (2.11) with the coefficients $a_i^{(1)}$ and $a_i^{(2)}$ from Eq. (4.30).

Since at $J/D = 3/4$ a change of the ground state occurs, the zero-temperature susceptibility is defined either by $a_7^{(2)}$ or $a_9^{(2)}$:

$$\chi_{xx}(T=0) = 2(\mu_B g)^2 \begin{cases} |a_7^{(2)}|, & \frac{J}{D} < \frac{3}{4} \\ |a_9^{(2)}|, & \frac{J}{D} > \frac{3}{4} \end{cases}. \tag{4.31}$$

In the limit of large and small J/D we obtain

$$\chi_{xx}(T=0) = (\mu_B g)^2 \frac{2}{D} \begin{cases} 1 + \frac{3}{8} \frac{J^2}{D^2}, & \frac{J}{D} \ll 1 \\ \frac{4}{81} \left(\frac{D}{J}\right)^3, & \frac{J}{D} \gg 1 \end{cases}. \tag{4.32}$$

It is interesting to note that the result Eq. (4.32) for the orthogonal cluster is one-half of that for the collinear cluster (Eq. (4.16)), a fact which can be explained on purely geometrical considerations.

In the case $J/D = 3/4$ the ground state is degenerate, and the coefficients a_7 and a_9 can be determined from the secular equation. As a result, no

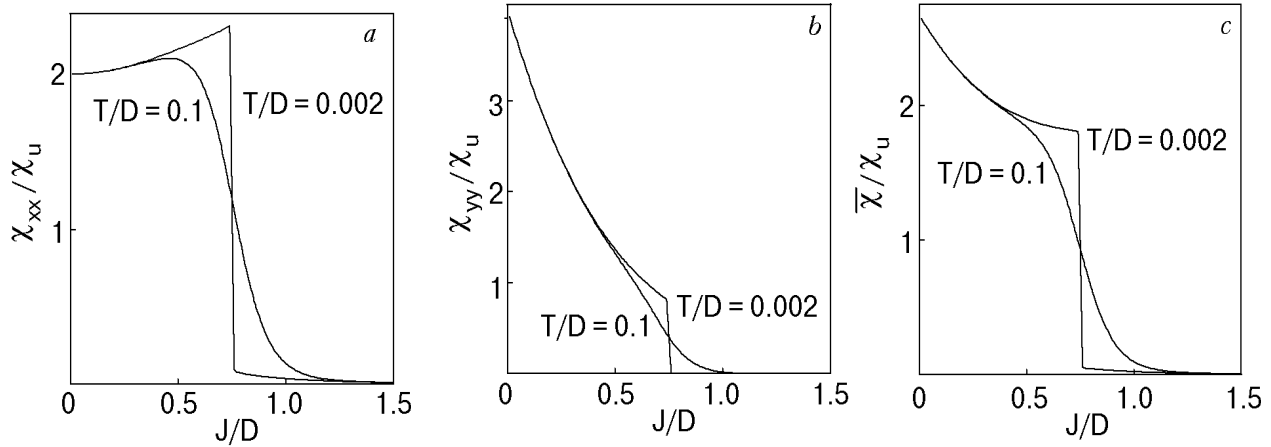


Fig. 3. Low-temperature magnetic susceptibility vs J/D : χ_{xx}/χ_u (a); χ_{yy}/χ_u (b); $\bar{\chi}/\chi_u$ (c), where $\chi_u = (g\mu_B)^2/D$.

$a_i^{(1)}$ coefficients appear for this degenerate case. The coefficients $a_7^{(2)}$ and $a_9^{(2)}$ take the form:

$$a_7^{(2)} = \frac{1}{2}(a_{7(0)}^{(2)} + a_{9(0)}^{(2)}) \pm \frac{1}{2} \left\{ (a_{7(0)}^{(2)} - a_{9(0)}^{(2)})^2 + 4 \left(l_9 - \frac{m_9}{\sqrt{2}} \right)^2 \right. \\ \left. \times \left[\frac{(l_4 + m_4)(l_4 l_7 - m_4 m_7)}{\left(\frac{D}{2} - \left(\frac{1}{4} D^2 + J^2 \right)^{1/2} \right)^{1/2} + \left(D^2 + J^2 \right)^{1/2}} + \frac{(l_5 + m_5)(l_5 l_7 - m_5 m_7)}{\left(\frac{D}{2} + \left(\frac{1}{4} D^2 + J^2 \right)^{1/2} \right)^{1/2} + \left(D^2 + J^2 \right)^{1/2}} \right] \right\}, \quad (4.33)$$

where $a_{7(0)}^{(2)}$, $a_{9(0)}^{(2)}$ are the coefficients for the nondegenerate case.

The zero-temperature susceptibility at the level-crossing point

$$\chi_{xx}(T=0) = (\mu_B g)^2 \left| a_{7(0)}^{(2)} + a_{9(0)}^{(2)} \right|. \quad (4.34)$$

As a result, the zero-temperature magnetic susceptibility given by Eqs. (4.31) and (4.34) is a nonmonotonic discontinuous function of J/D at $J/D = 3/4$. The jumps in the χ_{xx} vs J/D curve smears out with temperature. This peculiar behavior is displayed in Fig. 3,a.

χ_{yy} component of the magnetic susceptibility. Having found the second-order energy corrections to the nondegenerate levels from Eq. (4.2) and that to the degenerate levels from Eq. (4.3), we arrive at the following sets of coefficients $a_i^{(1)}$ and $a_i^{(2)}$:

$$a_1^{(1)} = a_6^{(1)} = a_7^{(1)} = a_8^{(1)} = a_9^{(1)} = 0;$$

$$a_2^{(1)} = \pm (l_2 m_4 - l_4 m_2); \quad a_3^{(1)} = \pm (l_3 m_5 - l_5 m_3); \quad (4.35)$$

$$a_1^{(2)} = -(a_6^{(2)} + a_7^{(2)}); \quad a_8^{(2)} = a_9^{(2)} = 0;$$

$$a_3^{(2)} = a_5^{(2)} = -a_2^{(2)} = -a_4^{(2)};$$

$$a_2^{(2)} = a_4^{(2)} = -\frac{1}{4} \frac{(l_3 m_4 - l_4 m_3)^2 + (l_2 m_5 - l_5 m_2)^2}{\sqrt{D^2/4 + J^2}};$$

$$a_6^{(2)} = 2 \frac{(l_6 - m_6)^2}{-J + \sqrt{D^2 + J^2}};$$

$$a_7^{(2)} = -2 \frac{(l_7 - m_7)^2}{J + \sqrt{D^2 + J^2}}. \quad (4.36)$$

In this case the coefficients a_7 and a_9 are unaffected by the crossing of the E_7 and E_9 levels, and Eq. (4.36) is universal for all J/D .

The zero-temperature susceptibility

$$\chi_{yy}(T=0) = 2(\mu_B g)^2 \begin{cases} |a_7^{(2)}|, & \frac{J}{D} < \frac{3}{4} \\ \frac{1}{2}|a_7^{(2)}|, & \frac{J}{D} = \frac{3}{4} \\ 0, & \frac{J}{D} > \frac{3}{4} \end{cases}. \quad (4.37)$$

The function Eq. (4.37) exhibits a jump at $J/D = 3/4$. In the limit of small J/D

$$\chi_{yy}(T=0) = 4(\mu_B g)^2 \frac{1}{D} \left(1 - 2 \frac{J}{D}\right). \quad (4.38)$$

For $J/D > 3/4$ $\chi_{yy}(T=0)$ is identically zero. The low-temperature behavior of χ_{yy} as a function of J/D is shown in Fig. 3,b. As can be seen, the jump in χ_{yy} at the crossing of the two lowest spin levels is smaller than the jump in χ_{xx} . The jump smears out with temperature.

Average susceptibility. The zero-temperature average susceptibility for the orthogonal cluster is given by

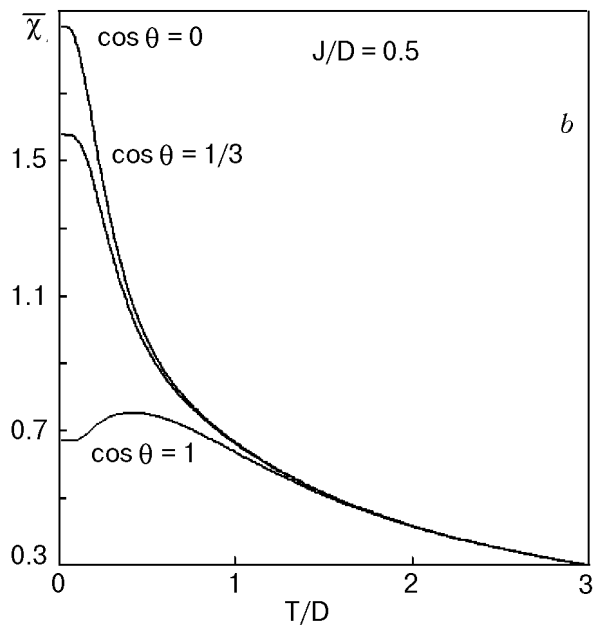
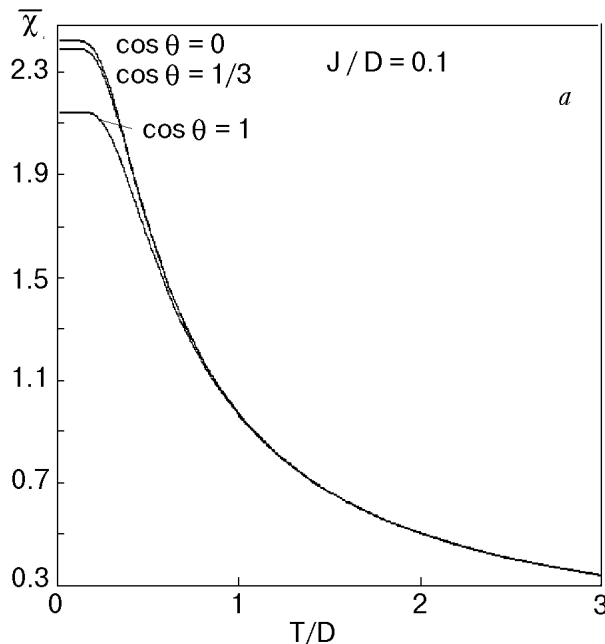


Fig. 4. Temperature dependence of the magnetic susceptibility of pair clusters of different geometry: $J/D = 0.1$ (a); $J/D = 0.5$ (b).

$$\bar{\chi}(T=0) = \frac{2}{3} (\mu_B g)^2 \begin{cases} 2|a_7^{(2)xx}| + |a_7^{(2)yy}|, & \frac{J}{D} < \frac{3}{4} \\ |a_7^{(2)xx}| + |a_9^{(2)yy}| + \frac{1}{2}|a_7^{(2)yy}|, & \frac{J}{D} = \frac{3}{4} \\ 2|a_9^{(2)xx}|, & \frac{J}{D} > \frac{3}{4} \end{cases} \quad (4.39)$$

In the limits small and large J/D we have

$$\bar{\chi}(T=0) = \frac{8}{3} (\mu_B g)^2 \frac{1}{D} \begin{cases} 1 - \frac{J}{D}, & \frac{J}{D} \ll 1 \\ \frac{1}{81} \left(\frac{D}{J}\right)^3, & \frac{J}{D} \gg 1. \end{cases} \quad (4.40)$$

The low-temperature behavior of the average susceptibility for the orthogonal cluster as a function of J/D is displayed in Fig. 3,c for two temperatures. As one can see, the jump at the crossing of the two lowest spin levels smears out with temperature.

Comparing Eq. (4.40) with the equation for the collinear cluster (Eq. (4.27)) we arrive an equation which displays the sensitivity of the low-temperature susceptibility of pair clusters to the angle between the molecular axes:

$$\left(\frac{\bar{\chi}_{\theta=0}}{\bar{\chi}_{\theta=\pi/2}} \right)_{T=0} = \begin{cases} 1 - \frac{J}{D}, & \frac{J}{D} \ll 1 \\ 4, & \frac{J}{D} \gg 1. \end{cases} \quad (4.41)$$

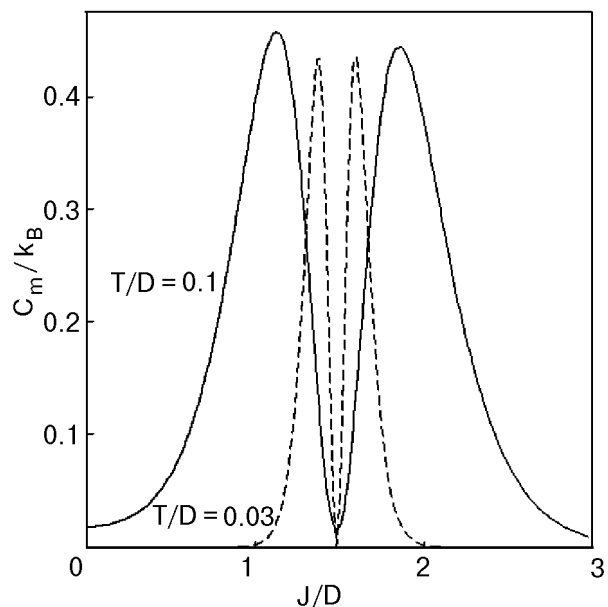


Fig. 5. Magnetic heat capacity.

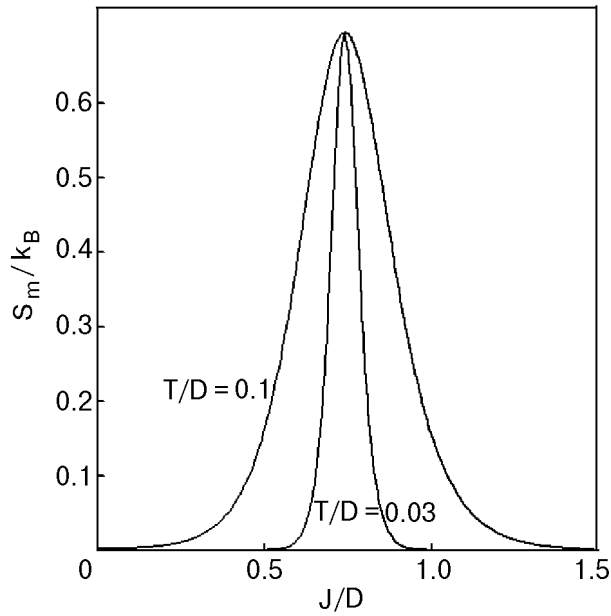


Fig. 6. Magnetic entropy.

5. Results and discussion

The magnetic susceptibility for an arbitrary angle between the molecular axes is given by Eq. (2.11) with the help of the coefficients a_i from Appendix C. Figure 4 gives a comparison of $\bar{\chi}$ vs T/D curves for three cluster geometries for different values of J/D . As can be seen, except at very small J/D , the low-temperature magnetic susceptibility is very sensitive to the cluster geometry. At zero temperature the angle dependence of the average susceptibility can be given in the analytical form [20]:

$$\bar{\chi}(\theta) = \frac{8}{3D} (\mu_B g)^2 \begin{cases} 1 - \frac{J}{D} (1 + \cos^2 \theta), & \frac{J}{D} \ll 1 \\ \frac{1}{81} \left(\frac{D}{J}\right)^3 (1+3 \cos^2 \theta), & \frac{J}{D} \gg 1. \end{cases} \quad (4.42)$$

Anomalies in the behavior of the magnetic heat capacities and magnetic entropy for the orthogonal cluster are shown in Figs. 5 and 6. A double-maximum Schottky-type anomaly in the magnetic heat capacity and a peak in the magnetic entropy are a consequence of the crossing of the lowest spin levels of the system with a change in J/D . In an experiment different values of the parameter J/D can be obtained by changing the pressure applied to the system. The same behavior of the magnetic entropy was observed experimentally in PrNi₅ in Ref. 21. In this case the level crossing takes place in a strong applied magnetic field.

As follows from Fig. 2, similar anomalies are characteristic for clusters with arbitrary θ since there is a minimum in the ΔE vs J/D curve, where ΔE is the gap between the two lowest spin levels. But in the absence of the crossing the anomalies are not so pronounced and the Schottky anomaly in the heat capacity has only one peak [3,7].

6. Conclusion

The magnetic properties of oxygen pair clusters were investigated theoretically for different cluster geometries which can be realized by doping molecular cryomatrices with oxygen. Anomalous temperature and pressure behavior of the magnetic susceptibility, heat capacity, and entropy is predicted. It is proposed to use these anomalies for studying the parameters characterizing the oxygen clusters and the parameters of the host matrix: the effective spin-figure interaction constant for the molecule in the matrix, the exchange parameter, and the number of impurity clusters in the solid solution. As a result, the data on the magnetic susceptibility may be used to extract information about the positional and orientational short-range order in the solid solution and about diffusion and clusterization processes in the system.

Appendix A

The orthonormal basis functions are

$$\begin{aligned} \Phi_1(B_{2g}) &= \frac{1}{\sqrt{2}}(\varphi_0 \psi_- + \varphi_- \psi_0); \\ \Phi_2(B_{1g}) &= \frac{1}{\sqrt{2}}(\varphi_0 \psi_+ - \varphi_+ \psi_0); \\ \Phi_3(B_{1g}) &= \frac{1}{\sqrt{2}}(\varphi_+ \psi_- + \varphi_- \psi_+); \\ \Phi_4(B_{3g}) &= \frac{1}{\sqrt{2}}(\varphi_0 \psi_+ + \varphi_+ \psi_0); \\ \Phi_5(B_{3g}) &= \frac{1}{\sqrt{2}}(\varphi_- \psi_+ - \varphi_+ \psi_-); \\ \Phi_6(A_{1g}) &= \varphi_0 \psi_0; \quad \Phi_7(A_{1g}) = \varphi_- \psi_-; \\ \Phi_8(A_{1g}) &= \varphi_+ \psi_+; \quad \Phi_9(A_{1g}) = \frac{1}{\sqrt{2}}(\varphi_0 \psi_- - \varphi_- \psi_0), \end{aligned} \quad (A1)$$

where $\varphi_0 = |0\rangle$, $\varphi_{\pm} = (1/\sqrt{2})(|1\rangle \pm |-1\rangle)$, and $|0\rangle$, $|\pm 1\rangle$ are eigenvectors of S_{1z_1} ; in the same

way $\Psi_0 = |0\rangle$, $\Psi_{\pm} = (1/\sqrt{2})(|1\rangle \pm |-1\rangle)$ are formed from eigenvectors of S_{2z_2} .

Appendix B

The unperturbed eigenvectors and eigenvalues are

$$\Psi(B_{2g}) = \Phi_1; \quad E_1 = D + J;$$

$$\Psi_2(B_{1g}) = l_2 \Phi_2 + m_2 \Phi_3;$$

$$E_2 = \frac{3}{2} D \mp \left(\frac{1}{4} D^2 + DJ \cos \theta + J^2 \right)^{1/2};$$

$$l_2 = \frac{J}{D} \sin \theta \left\{ \frac{J^2}{D^2} \sin^2 \theta + \left(1 - \frac{J}{D} \cos \theta - \frac{E_2}{D} \right)^2 \right\}^{-1/2};$$

$$m_2 = \pm \left(1 - l_2^2 \right)^{1/2}; \quad \Psi_4(B_{3g}) = l_4 \Phi_4 + m_4 \Phi_5;$$

$$E_4 = \frac{3}{2} D \mp \left(\frac{1}{4} D^2 - DJ \cos \theta + J^2 \right)^{1/2};$$

$$l_4 = \frac{J}{D} \sin \theta \left\{ \frac{J^2}{D^2} \sin^2 \theta + \left(1 + \frac{J}{D} \cos \theta - \frac{E_4}{D} \right)^2 \right\}^{-1/2};$$

$$m_4 = \pm \left(1 - l_4^2 \right)^{1/2}.$$

The remaining four eigenvectors and eigenvalues

$$\Psi_i(A_{1g}) = \sum_6 c_{ik}(J/D, \cos \theta) \Phi_k;$$

$$E_i = E_i(J/D, \cos \theta), \quad i = 6, 7, 8, 9$$

belonging to the A_{1g} representation can be found in the general case only numerically as the result of a diagonalization of $\mathcal{H}_{A_{1g}}$ (Eq. (3.6)).

Explicit equations for the eigenfunctions and eigenvalues belonging to the fourfold representation A_{1g} for the two limiting cases of the collinear and orthogonal clusters are given below.

Collinear cluster ($\cos \theta = 1$)

$$\Psi_6(A_{1g}) = \frac{1}{\sqrt{2}} (\Phi_7 + \Phi_8); \quad E_6^0 = 2D + J;$$

$$\Psi_7(A_{1g}) = \left(\frac{J^2}{D^2} + \frac{(E_7^0)^2}{2D^2} \right)^{-1/2} \left\{ \frac{J}{D} \Phi_6 - \frac{E_7^0}{2D} (\Phi_7 - \Phi_8) \right\};$$

$$E_7 = D - \frac{J}{2} \pm \left(D^2 - DJ + \frac{9}{4} J^2 \right)^{1/2};$$

$$\Psi_9(A_{1g}) = \Phi_9; \quad E_9^0 = D - J.$$

Orthogonal cluster ($\cos \theta = 0$)

$$\Psi_6(A_{1g}) = l_6 \Phi_6 + m_6 \Phi_7; \quad E_6 = D \pm \sqrt{D^2 + J^2};$$

$$l_6 = \frac{J}{D} \left\{ \left(\frac{J}{D} \right)^2 + \left[\left(1 + \left(\frac{J}{D} \right)^2 \right)^{1/2} \pm 1 \right] \right\}^{-1/2};$$

$$m_6 = \mp \sqrt{1 - l_6^2}; \quad \Psi_8(A_{1g}) = l_8 \Phi_8 + m_8 \Phi_9;$$

$$E_8 = \frac{3}{2} D - \frac{1}{2} J \pm \left(\frac{1}{4} D^2 + \frac{1}{2} DJ + \frac{9}{4} J^2 \right)^{1/2};$$

$$l_8 = \frac{J}{D} \left\{ \frac{J^2}{D^2} + \right.$$

$$\left. + \frac{1}{2} \left[\frac{1 + J/D}{2} \mp \left(\frac{1}{4} + \frac{J}{2D} + \frac{9J^2}{4D^2} \right)^{1/2} \right] \right\}^{-1/2};$$

$$m_8 = \mp \left(1 - l_8^2 \right)^{1/2}.$$

Appendix C

Coefficients $a_i^{(2)}$ for the general case

In a general case all coefficients $a_i^{(1)}$ are zero, except special cases of J/D when there is an additional (accidental) degeneracy in the spectrum. The coefficients $a_i^{(2)}$ are different for different components of the susceptibility. The sets of $a_i^{(2)}$ coefficients for χ_{xx} , χ_{yy} , and χ_{zz} , respectively, are as follows.

χ_{xx} :

$$a_1^{(2)} = - (a_2^{(2)} + a_3^{(2)}) ; \quad a_2^{(2)} = \frac{(l_2 \sin \frac{\theta}{2} - m_2 \cos \frac{\theta}{2})^2}{E_1 - E_2} ;$$

$$a_4^{(2)} = \sum_{i=6}^9 \frac{1}{E_i - E_5} \left\{ \left(\sqrt{2} c_{i6} \cos \frac{\theta}{2} + \sqrt{2} c_{i8} \cos \frac{\theta}{2} - c_{i9} \sin \frac{\theta}{2} \right) l_4 + \left(-\sqrt{2} c_{i7} \sin \frac{\theta}{2} + \sqrt{2} c_{i8} \sin \frac{\theta}{2} - c_{i9} \cos \frac{\theta}{2} \right) m_4 \right\}^2 ;$$

$$a_k = \sum_{i=6,7} \frac{1}{E_k - E_i} \left\{ \left(\sqrt{2} c_{k6} \cos \frac{\theta}{2} + \sqrt{2} c_{k8} \cos \frac{\theta}{2} - c_{k9} \sin \frac{\theta}{2} \right) l_i + \left(-\sqrt{2} c_{k7} \sin \frac{\theta}{2} + \sqrt{2} c_{k8} \sin \frac{\theta}{2} - c_{k9} \cos \frac{\theta}{2} \right) m_i \right\}^2 ; \quad k = 6, \dots, 9.$$

Here c_{ik} are components of the eigenvectors belonging to the eigenvalues of Eq. (3.6).

χ_{yy} :

$$a_1^{(2)} = - (a_6^{(2)} + a_7^{(2)} + a_8^{(2)} + a_9^{(2)}) ; \quad a_2^{(2)} = \sum_{i=4,5} \frac{(l_i m_2 - m_i l_2)^2}{E_i - E_2} ; \quad a_4^{(2)} = \sum_{i=2,3} \frac{(l_i m_4 - m_i l_4)^2}{E_i - E_5} ;$$

$$a_k = 2 \frac{(c_{k6} - c_{k7})^2}{E_k - E_1} \quad (k = 6, \dots, 9).$$

χ_{zz} :

$$a_1^{(2)} = - (a_4^{(2)} + a_5^{(2)}) ;$$

$$a_2^{(2)} = \sum_{i=6}^9 \frac{1}{E_2 - E_i} \left\{ \left(\sqrt{2} c_{i6} \sin \frac{\theta}{2} - \sqrt{2} c_{i8} \sin \frac{\theta}{2} + c_{i9} \cos \frac{\theta}{2} \right) l_2 + \left(\sqrt{2} c_{i7} \cos \frac{\theta}{2} + \sqrt{2} c_{i8} \cos \frac{\theta}{2} - c_{i9} \sin \frac{\theta}{2} \right) m_4 \right\}^2 ;$$

$$a_4^{(2)} = \frac{(l_4 \sin \frac{\theta}{2} - m_4 \cos \frac{\theta}{2})^2}{E_1 - E_2} ;$$

$$a_i^{(2)} = \sum_{k=2,3} \frac{1}{E_i - E_k} \left\{ \left(\sqrt{2} c_{i6} \sin \frac{\theta}{2} - \sqrt{2} c_{i8} \sin \frac{\theta}{2} + c_{i9} \cos \frac{\theta}{2} \right) l_k + \left(\sqrt{2} c_{i7} \cos \frac{\theta}{2} + \sqrt{2} c_{i8} \cos \frac{\theta}{2} - c_{i9} \sin \frac{\theta}{2} \right) m_k \right\}^2$$

($i = 6, \dots, 9$).

Acknowledgments

The work was supported in part by the Polish Committee for Scientific Research through Grant No. 2 PO3B 14210.

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