Russian Chemical Bulletin, International Edition, Vol. 60, No. 12, pp. 2485—2489, December, 2011

# A matrix method for calculating the magnetic properties of $Co^{2+}$ complex ions

**E. F. Kustov,[a] V. M. Novotortsev,[b] I. L. Eremenko,[b] and E. O. Goncharov[a]★**

[a]*Moscow Power Engineering Institute (Technical University),*
*14 ul. Krasnokazarmennaya, 111250 Moscow, Russian Federation.*
*Fax: +7 (495) 362 8938. E-mail: goncharoveo@list.ru*
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
*31 Leninsky prosp., 117907 Moscow, Russian Federation.*
*Fax: +7 (495) 954 1279. E-mail: vmnov@igic.ras.ru*

A matrix method for calculating of the magnetic properties of $Co^{2+}$ complex ions is proposed. The method involves calculations of a full matrix of all interactions existing in the ion. The theoretical results obtained by this method more accurately describe the observed experimental values of magnetic parameters of mononuclear complexes with $Co^{2+}$ ions.

**Key words:** matrix method of calculations, magnetic moment, cobalt ion, spin-orbit interaction, electrostatic interaction, interaction with intramolecular field.

Research on the magnetic properties enables more detailed studies of the structural features of magnetoactive coordination compounds. Having known the effective magnetic moments, magnetic susceptibilities, and their temperature dependences, one can evaluate the oxidation state and the spin state of a metal, to assess the nature of intra- and intermolecular interactions between paramagnetic centers, the geometry, as well as the symmetry of mono- and polynuclear complexes.

In this work, we used the fundamentals of theory of magnetism in transition-metal coordination compounds[1,2] as well as new results obtained based on the direct methods of matrix calculations of the magnetic moments and magnetic susceptibilities without using the van Vleck approximation. The matrix method of calculations of the magnetic properties of paramagnetic transition-metal ions implies solution of a full matrix of all interactions in the ion (electrostatic interaction between electrons, spin-orbit interaction, and interactions with intramolecular field (IMF) and external magnetic field). The principles of this approach have been reported recently.[3] Theoretical consideration of the key magnetochemical regularities is based on construction of molecular orbitals and a hybridization scheme of the orbits of magnetic atoms and ligands. The molecular orbitals of s-, p-, and d-electrons in coordination polyhedra of different symmetry are constructed using the orbit system of different complexes and complex molecules[4] in which the distribution of atoms in a molecule, complex, or clusters is determined by concentric (nested) orbits with their own coordination numbers. This system is used in the matrix calculations of the magnetic properties of complex ions.[5,6]

For ions with the $d^7$ electronic configuration, a 120×120 matrix allows one to calculate the magnetic properties depending on the parameters of electrostatic and spin-orbit interactions, parameters of the IMF potential, and thirteen parameters of lower symmetry. The last-mentioned group of parameters includes the second-order parameters $A_{20}$, $A_{22}$, $A_{2-2}$, $A_{21}$, and $A_{2-1}$.

The main idea of the matrix method of calculations of the magnetic properties in the van Vleck approximation[7] is as follows: this approximation is based on the assumption that the quantum numbers of the total momentum $J$ and its projections $J_m$ are "good" quantum numbers. The vectors $J_m$ interact with the magnetic field and the energy of this interaction is proportional to $J_m$. This enables summation of the magnetic moments using the squared projections of the total momentum $J_m$ and determination of the total magnetic moment from the relation

$$\mu_J^2 = \beta^2 g(SLJ)^2 J(J+1) \quad (1)$$

and makes it possible to derive the expression for the magnetic susceptibility using the temperature averaging of the magnetic moments over all states with different values of the momentum $J$ (for details, see Ref. 8)

However, the observed magnetic moments of $Co^{2+}$ compounds are often higher than the value obtained using relation (1) in the van Vleck approximation. This contradiction is eliminated when using a full matrix of interactions of the $Co^{2+}$ ion and calculating the magnetic moment value using this matrix.

---

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2437—2441, December, 2011.

The full matrix of all states of the $d^7$ configuration includes interactions of all states, and the function of state of each energy level is determined by a linear combination of the functions of states with different momentum $J_m$. In this approach, the quantum numbers of a free atom can no longer be used.

Figure 1 shows the squared magnetic moment values of $Co^{2+}$ ion with the $d^7$ electronic configuration of the $^4F_J$ ground state at different values of the spin-orbit interaction constants $\zeta$ and the IMF parameters $Dq$ and $A_{20}$.

The values corresponding to the approximation *1* in Fig. 1 represent the squared magnetic moments calculated in the van Vleck approximation (1) for $J$ = 9/2, 7/2, 5/2, 3/2. The values corresponding to the approximation *2* represent the squared magnetic moments calculated by the matrix method taking into account only electrostatic interaction. Electrostatic interaction determined from full-matrix calculations leads to mixing of the quantum numbers $S$ and $L$ so that none of them can be used individually for characterization of states. Therefore, the $g(SLJ)$-factor is also a combination of the factors of splitting of different $SL$ multiplets. This is ignored in the van Vleck approximation.

The values corresponding to the approximation *3* (see Fig. 1) represent the squared magnetic moments calculated taking into account the spin-orbit interaction. As can be seen, the order of magnitude of the corresponding squared magnetic moments is the same as in the van Vleck approximation; however, the numerical values of the moments are different. The ground-state magnetic moment $\mu^2_{9/2}$ increases from 44 to 50, but the $\mu^2_{7/2}$, $\mu^2_{5/2}$, and $\mu^2_{3/2}$ values decrease. These changes are shown in Fig. 2 for the squared projections $(J_m)^2$ for all $J$ levels of the $^4F_J$ multiplet of the $Co^{2+}$ ion. Relationships between the squared projections $J_m$ of the states with $J = 9/2$ are listed in Table 1. These numbers for the projections with the number $m$ from ±1/2 to ±9/2 should be equal to the corresponding numbers $(2m)^2$ (see row 2 in Table 1); however, they actually differ from the values for free atom. Cobalt ions in different states interact with other ions in different manner and the "pure" projection values change. For instance, the component $m = 1/2$ equals $m = 1/2 \cdot \sqrt{1.3}$. The same is observed for other components of the momentum $J = 9/2$. For some components, these values are larger than the values for free atom; for other components, they are smaller. This is due to mixing of different components $J_m$ owing to the interaction with higher states. From the data in Fig. 2 it follows that the effect of mixing of states becomes more pronounced for the excited states with $J$ = 7/2, 5/2, and 3/2. Mixing of states leads to different Zeeman splitting values, which violates the system of equidistant energy levels used in the van Vleck approximation.

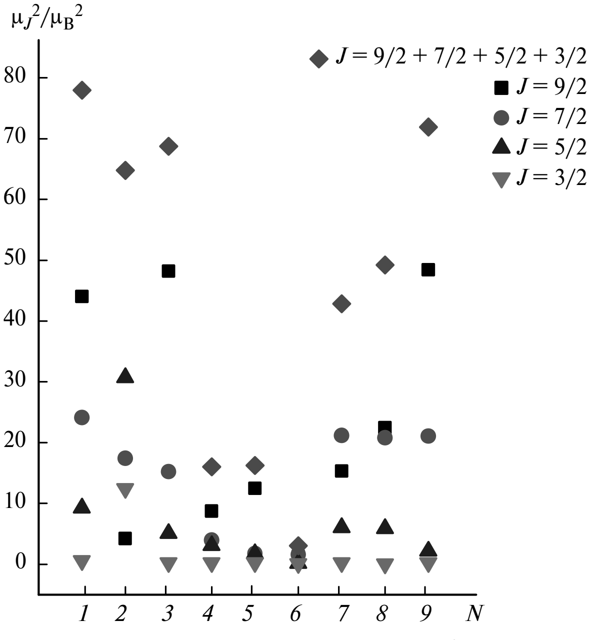

**Fig. 1.** Squared magnetic moment values of $Co^{2+}$ ion ($d^7$ electronic configuration, $^4F_J$ ground state) at different values of the spin-orbit interaction constant $\xi$ and intramolecular field parameters $Dq$ and $A_{20}$ (in $cm^{-1}$): the van Vleck approximation (*1*); $\xi = 0$, $Dq = 0$, $A_{20} = 0$ (*2*); $\xi = -525$, $Dq = 0$, $A_{20} = 0$ (*3*); $\xi = -525$, $Dq = 10$, $A_{20} = 0$ (*4*); $\xi = -525$, $Dq = 100$, $A_{20} = 0$ (*5*); $\xi = -525$, $Dq = 1000$, $A_{20} = 0$ (*6*); $\xi = -525$, $Dq = 0$, $A_{20} = 10$ (*7*); $\xi = -525$, $Dq = 0$, $A_{20} = 50$ (*8*); $\xi = -525$, $Dq = 0$, $A_{20} = 100$ (*9*); $N$ is the number of approximation.

The values corresponding to the approximation *4* (see Fig. 1) represent the squared magnetic moments calculated taking into account the spin-orbit interaction and IMF with cubic symmetry and the parameter $Dq = 10\ cm^{-1}$. The magnetic moment of each state and the sum of the moments abruptly decrease due to splitting of the $J$-states under the action of IMF. For instance, the state with $J = 9/2$ is split into three levels (two quartets G´ and one doublet E´) with their own momentum values. The magnetic moments of the ground-state level G´ with the states $m$ = ±3/2, ±1/2, and those of the second and third levels G´ and E´ are shown in Fig. 3. The effect of highly symmetrical IMF (here, it has a cubic symmetry) changes the ratios of the magnetic moments and leads to formation of new states with much smaller magnetic moments.

**Table 1.** Ratios of the magnetic moments of the states with $J = 9/2$ with different $m$ values and the states with $J = 9/2$ and $m = 1/2$ in the presence of spin-orbit interaction

| $m$ | $(\mu_m/\mu_{1/2})^2$ | Calculated by the matrix method | $m$ | $(\mu_m/\mu_{1/2})^2$ | Calculated by the matrix method |
|---|---|---|---|---|---|
| −1/2 | 1 | 1.0 | 5/2 | 25 | 24.7 |
| 1/2 | 1 | 1.3 | −7/2 | 49 | 46.8 |
| −3/2 | 9 | 9.1 | 7/2 | 49 | 48.1 |
| 3/2 | 9 | 9.1 | −9/2 | 81 | 81.7 |
| −5/2 | 25 | 25.2 | 9/2 | 81 | 81.7 |

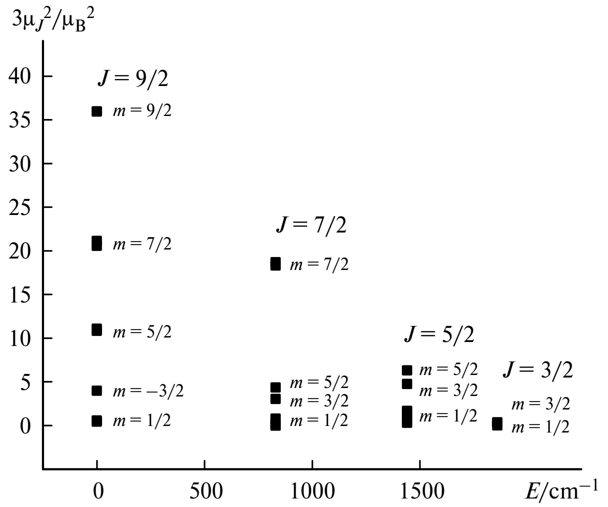

**Fig. 2.** Squared magnetic moment values of $Co^{2+}$ ion ($d^7$ electronic configuration, $^4F_J$ ground state) at the electrostatic interaction parameters $F_2$ = 77206 cm$^{-1}$ and $F_4$ = 53088 cm$^{-1}$, spin-orbit interaction constant $\xi$ = –525 cm$^{-1}$, and intramolecular field parameters $Dq$ = 0 cm$^{-1}$ and $A_{20}$ = 0 cm$^{-1}$; $E$ is energy.

The magnetic properties weaken as the IMF with cubic symmetry becomes stronger (see Fig. 1, approximations *5* and *6*).

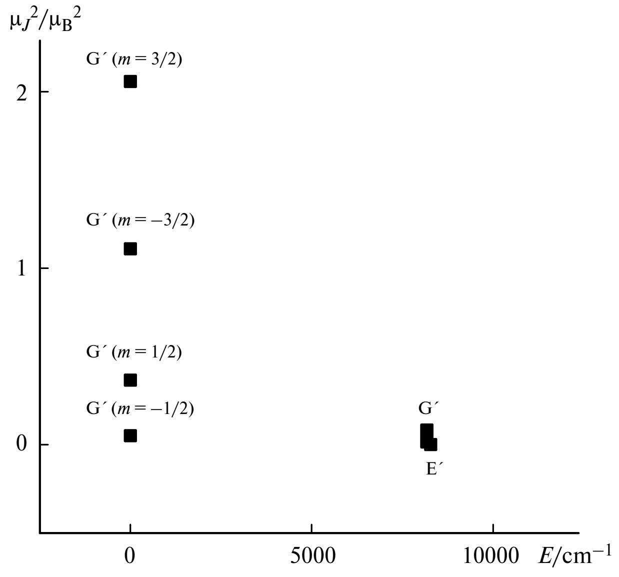

**Fig. 3.** Squared magnetic moment values of $Co^{2+}$ ion ($d^7$ electronic configuration, $^4F_{9/2}$ state) at the electrostatic interaction parameters $F_2$ = 77206 cm$^{-1}$ and $F_4$ = 53088 cm$^{-1}$, spin-orbit interaction constant $\xi$ = –525 cm$^{-1}$, and intramolecular field parameters $Dq$ = 1000 cm$^{-1}$ and $A_{20}$ = 0 cm$^{-1}$.

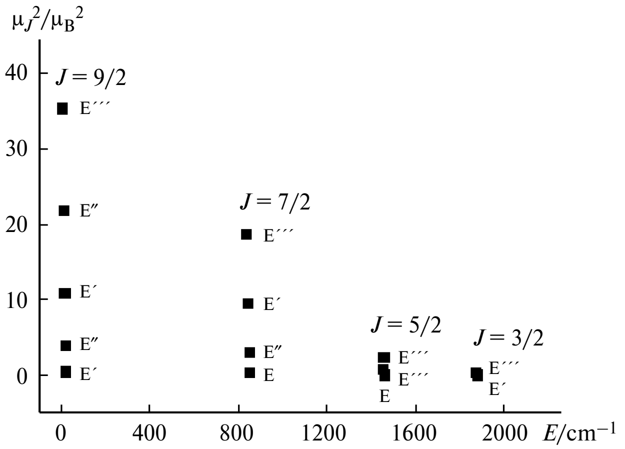

**Fig. 4.** Squared magnetic moment values of $Co^{2+}$ ion ($d^7$ electronic configuration, $^4F_J$ ground state) at the electrostatic interaction parameters $F_2$ = 77206 cm$^{-1}$ and $F_4$ = 53088 cm$^{-1}$, spin-orbit interaction constant $\xi$ = –525 cm$^{-1}$, and intramolecular field parameters $Dq$ = 0 cm$^{-1}$ and $A_{20}$ = 100 cm$^{-1}$.

We have found that the abnormal increase in the magnetic moment of $Co^{2+}$ ion can be explained by the presence of low-symmetry components of the IMF. The values corresponding to the approximations *7*, *8*, and *9* (see Fig. 1) show a maximum increase in the magnetic moment at $A_{20}$ = 100 cm$^{-1}$. Figure 4 presents the squared magnetic moment of $Co^{2+}$ ion at the axial IMF parameter $A_{20}$ = 100 cm$^{-1}$ (Table 2).

According to our matrix calculations, in a magnetic field the energy difference between the neighboring Zeeman levels decreases under the action of intramolecular field, which leads to an increase in the magnetic moments of all these states. These changes in the Zeeman splitting of energy levels represent the source of the third contradiction to the van Vleck approximation.

The matrix method was used to explain the magnetic properties of the following mono- and dinuclear coordination compounds of cobalt(II)[9]: $Co(dipy)_2(OOCCMe_3)_2$, $Co(dipy)(OOCCMe_3)_2$, $Co(dipy)(H_2O)(OOCCMe_3)_2$, and $Co(dipy)(N\text{-}Ph\text{-}opda)(OOCCMe_3)_2$, where dipy is 2,2′-dipyridyl and N-Ph-opda is *N*-phenyl-*o*-phenylenediamine.

When calculating the magnetic properties by the matrix method, one should first define the parameters of electrostatic and spin-orbit interactions in such a manner that the theoretical values describing the energy band structure

**Table 2.** Ratios of the magnetic moments of the states with $J$ = 9/2 with different $m$ values and the states with $J$ = 9/2 and $m$ = 1/2 at axial intramolecular field parameter $A_{20}$ = 100 cm$^{-1}$

| $m$ | $(\mu_m/\mu_{1/2})^2$ | Calculated by the matrix method | $m$ | $(\mu_m/\mu_{1/2})^2$ | Calculated by the matrix method |
|---|---|---|---|---|---|
| –1/2 | 1 | 0.89 | 5/2 | 25 | 21.87 |
| 1/2 | 1 | 0.89 | –7/2 | 49 | 43.64 |
| –3/2 | 9 | 8.01 | 7/2 | 49 | 43.64 |
| 3/2 | 9 | 8.01 | –9/2 | 81 | 70.91 |
| –5/2 | 25 | 21.87 | 9/2 | 81 | 70.91 |

is in good agreement with the reference data for $Co^{2+}$ ion.[10] Mention may be made that the parameters of electrostatic and spin-orbit interactions depend only slightly on the coordination environment of the cobalt ion and on external conditions (temperature, *etc.*). The theoretical and experimental magnetic moment values and their temperature dependences for four cobalt complexes were compared using an original simulation program. The error in the theoretical results was estimated by the least squares method; it was at most 15% on the average.

The experimental temperature dependences of the magnetic moments of the complexes under study were approximated by the theoretical values obtained by fitting the IMF parameter values. It was found that the magnetic properties of the $Co^{2+}$ ion in the complexes under study can be described by three IMF parameters $A_{20}$, $A_{22}$, and $A_{21}$. According to calculations, other second-order IMF parameters are equal to zero because even if their values are small, the theoretical values of the magnetic moments become significantly different from the experimental ones. The results of calculations of the magnetic moments of $Co^{2+}$ ion in different molecules by the least-squares method and determination of a complete set of parameters of intramolecular interactions are presented in Figs 5—8. It should be noted that the theoretical and experimental magnetic moment values of the complex shown in Fig. 6 deviate from one another due to internuclear exchange interactions at low temperatures.

Based on the results obtained, it was shown that the magnetic moments calculated in the van Vleck approximation decrease under the action of highly symmetrical intramolecular fields. An abrupt increase of the magnetic moments (up to doubling) was found for the molecules with axial (tetragonal, trigonal, or hexagonal) symmetry. Enhanced magnetism of cobalt is due to the effect of the IMF with second-order harmonics. The matrix method of

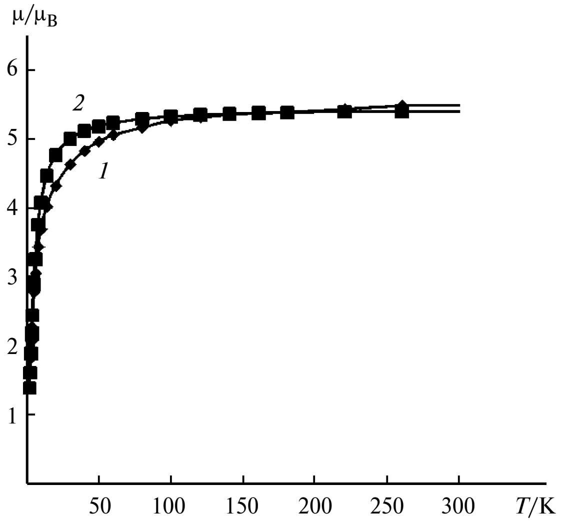

**Fig. 5.** Magnetic moment of $Co(dipy)_2(Piv)_2$ in the temperature range 2—301 K: $\mu_{eff}$ values (*1*) and theoretical values (*2*) at the intramolecular field parameters $A_{20} = -35.2\ cm^{-1}$, $A_{22} = 6.2\ cm^{-1}$, and $A_{21} = 12.2\ cm^{-1}$.

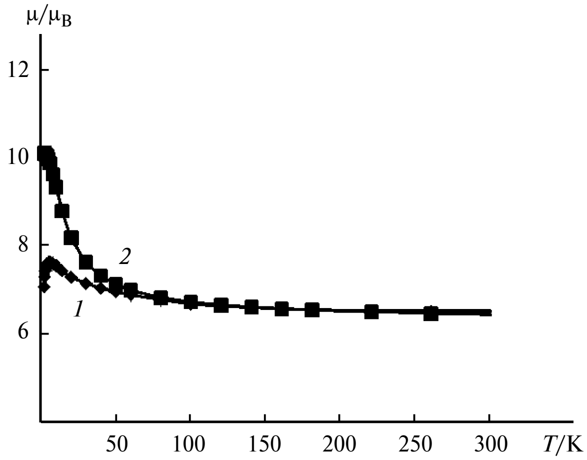

**Fig. 6.** Magnetic moment of $Co(dipy)(Piv)_2$ in the temperature range 2—301 K: $\mu_{eff}$ values (*1*) and theoretical values (*2*) at the intramolecular field parameters $A_{20} = 116\ cm^{-1}$, $A_{22} = 7\ cm^{-1}$, and $A_{21} = 34\ cm^{-1}$.

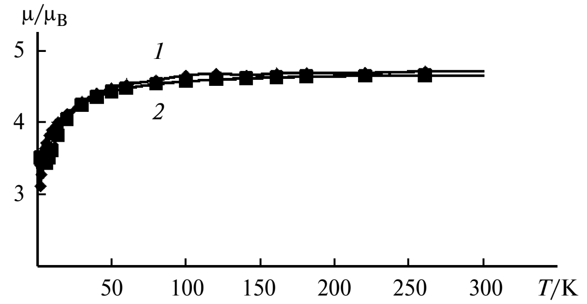

**Fig. 7.** Magnetic moment of $Co(dipy)(H_2O)(Piv)_2$ in the temperature range 2—301 K: $\mu_{eff}$ values (*1*) and theoretical values (*2*) at the intramolecular field parameters $A_{20} = -40\ cm^{-1}$, $A_{22} = 35\ cm^{-1}$, and $A_{21} = 35\ cm^{-1}$.

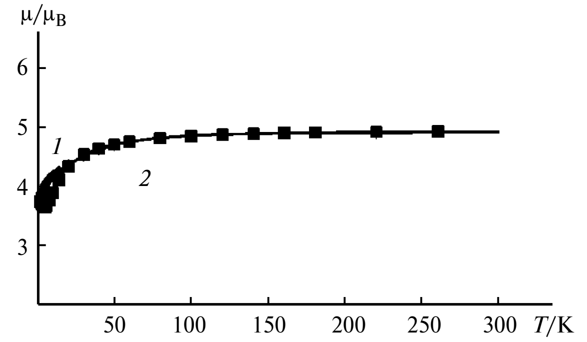

**Fig. 8.** Magnetic moment of $Co(dipy)(N\text{-}Ph\text{-}opda)(Piv)_2$ in the temperature range 2—301 K: $\mu_{eff}$ values (*1*) and theoretical values (*2*) at the intramolecular field parameters $A_{20} = -37\ cm^{-1}$, $A_{22} = 29\ cm^{-1}$, and $A_{21} = 34\ cm^{-1}$.

calculations provides an explanation for the dependence of the magnetic moment and magnetic susceptibility in the temperature range 50—300 K; deviation of the experimental curve from the theoretical curve in the temperature range 2—50 K can be explained by the presence of exchange interactions.

This work was financially supported by the Council on Grants at the President of the Russian Federation (Program of State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-8503.2010.3), the Presidium of the Russian Academy of Sciences (Program No. 7), and the Chemistry and Materials Science Division of the Russian Academy of Sciences (Program No. 7).

## References

1. V. T. Kalinnikov, Yu. V. Rakitin, *Vvedenie v magnetokhimiyu* [*Introduction to Magnetochemistry*], Nauka, Moscow, 1980, 302 pp. (in Russian).
2. Yu. V. Rakitin, V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St. Petersburg, 1994, 272 pp. (in Russian).
3. E. F. Kustov, V. T. Kalinnikov, V. M. Novotortsev, *Russ. J. Inorg. Chem.*, 2009, **54**, 2107.
4. E. F. Kustov, *Dokl. Akad. Nauk*, 2011, **438**, 631 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 2011, **438**, Pt. 2, 105].
5. E. F. Kustov, *J. Compt. Theor. Nanosci.*, 2008, **5**, 2144.
6. E. F. Kustov, *J. Compt. Theor. Nanosci.*, 2009, **6**, 692.
7. L. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London, 1932, 384 pp.
8. W. Nolting, A. Ramakanth, *Quantum Theory of Magnetism*, Springer-Verlag, Heidelberg—Dordrecht—London—New York, 2009, p. 166.
9. A. A. Sidorov, D.Sc. (Chem.) Thesis, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 2002, 221 pp. (in Russian).
10. NIST Atomic Spectra Database Levels Data. -URL: http://physics.nist.gov/PhysRefData/ASD/levels_form.html. Retrieval date: 20.10.2010.

*Received September 14, 2011;*
*in revised form November 14, 2011*