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Magnetic properties and nanostructural changes in the diamagnetic ionic systems

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The investigation of magnetic properties of ionic crystalline systems, in which the total electron spin equals zero, is one of the universal methods of studying the character of chemical bonding in such materials. In this paper is made an evaluation of the influence of deformation and overlapping of ionic clouds in the crystalline field. We are interested in a correct evaluation of the ionic deformation, in the same time being interested in the determination of the overlapping contribution for evaluations of magnetic properties, diamagnetic and paramagnetic too. For this purpose was developped a theoretical model, which allows us to make all investigations on ionic-covalent and covalent-ionic compounds. The results are in a good agreement with experimental investigations made on such systems, being superior to the results obtained by other methods and models. In this work is presented a correlation formula between total magnetic susceptibility χ and paramagneticVanVleck susceptibility χ_{para}. Through the model proposed it is possible to find a correlation between the magnetic properties and the nanostructural configuration of the deformations of outer electronic clouds and the overlapping of these ions.

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1. Introduction

Getting to know the behaviour of ionic diamagnetic crystalline compounds in the magnetic field supposes a lot of difficulties because the ions are diamagnetic in their free state. In the crystalline field the Langevin susceptibility of the free ions is modified, and in the same time, a paramagnetic Van Vleck susceptibility arises [1,2]. Thus, such a system involves a diamagnetic susceptibility χ_{dia} and an induced Van Vleck paramagnetic susceptibility χ_{para}, both being thermal and magnetical independent, so their separately determination by experiment being quite impossible. Their calculation implies many complications because they are not separately gauge origin invariant [3]. Therefore we introduced the magnetization coefficients of diamagnetic ions by passing from free state to crystalline state in the magnetic field. They are suggestively expressing the change of the charge density for free ions, when they are going to the crystalline field.

The experimental data for susceptibility of the lattice χ are used to evaluate some parameters of the chemical bond in the same time with the results of the orbital overlapping model of radial deformable ions in crystalline field. These data can be expressed as a sum of two components, the Langevin diamagnetism, χ_{dia} and the Van Vleck paramagnetism, χ_{para}:

$$\chi = \chi_{dia} + \chi_{para} = \chi_{d,core} + \chi_{d,val} + \chi_{para} \qquad (1)$$

where the Langevin susceptibility χ_{dia} is given as a sum of the core-electron component $\chi_{d,core}$ and the Langevin contribution of the outer electronic clouds $\chi_{d,val}$, deformable in crystalline field and responsible of the Van Vleck paramagnetism χ_{para}. Both, $\chi_{d,val}$ and χ_{para} are depending on the details of chemical bonding in the solid. The separation of the magnetic susceptibility into the Langevin diamagnetic and Van Vleck paramagnetic terms makes the relationship between the magnetic susceptibility and the chemical bond. So, in magnetic field, the crystalline state there are five important susceptibility components: χ, χ_{dia}, $\chi_{d,core}$, $\chi_{d,val}$ and χ_{para} every one of them being important in determination of the magnetic properties and the chemical bonding. We can obtain χ from literature data [5,6], χ_{dia} from one of the known models χ_{para} within the model of overlapping radial deformable ions in crystalline field, $\chi_{d,core}$ and $\chi_{d,val}$ determined using the correction coefficients ionic-covalent systems [7].

2. Theoretical model

The diamagnetic component of magnetic susceptibility of the valence electronic clouds which are responsible for chemical bonding is determined by the radial deformation, very important for the emergency of the induced paramagnetic vortex evaluated by the Van Vleck susceptibility χ_{para}.We consider that the core-electron diamagnetism varies negligibly when passing from the isolated state in the atom to the bound one in crystals. Therefore the $\chi_{d,core}$ of the ions, given in Selwood [5], and calculated by us [8], are employed to sufficient accuracy while calculating the diamagnetic susceptibility of crystals. The diamagnetic component of the magnetic susceptibility of the valence electron $\chi_{d,val}$, which is responsible along with the Van Vleck paramagnetic component of magnetic susceptibility χ_{para} for chemical bonding in diamagnetic crystalline systems (ionic-covalent or covalent-ionic) depends not only on the square of ionic radius, but also on the distance between atoms taking part in the bond.

The Van Vleck paramagnetic term χ_{para} is connected with the quantum-mechanical effect of virtual deformation of the electron clouds under the action of magnetic field [1], due to asymmetry of these electrons, when atoms are structuring as crystalline network of ions. The paramagnetic contribution to the magnetic susceptibility in ionic-covalent crystals depends strongly on the character of bond in crystals, and its energy characteristics.

Both $\chi_{d,val}$ and χ_{para} depend on the details of chemical bonding in the solid crystalline state. The separation of the magnetic susceptibility of lattice into the Langevin diamagnetic and the Van Vleck paramagnetic terms allows us to determine the character of chemical bond in crystals. The magnetic coefficients, radial, orbital and effective introduced can determine the nanostructural changes at the level of the electronic clouds of the ions in crystalline field. The character of the chemical bond determines the degree of asymmetry of electronic clouds. The absolute value of ratio of paramagnetic to diamagnetic components χ_{para}/χ_{dia} could serve as a qualitative measure of the covalency parameter λ_i, or ionicity parameter f_i=1-λ_i (the pure covalent systems with λ_i=1 has the ratio value equal to 1).

The ionic and covalent concepts are useful when they are defined in terms of the density distribution. In an idealized model of ionic bond there is no overlap or shared density. Instead the complete transfer of charge will increase the screening contribution of the anions by unity and the decrease that of caution by unity. The covalent bond is defined as one in which the transfer of charge is total by decreasing of both distribution of the charge. Between these situations we have the ionic-covalent and covalent-ionic chemical bond. The Van Vleck paramagnetic component of magnetic susceptibility χ_{para} is more closely connected with chemical bonding. [9].

When the atoms are passing from free state in crystalline state in a magnetic applied field, are observed some nanostructural changes at the level of outer radial deformable clouds in the crystalline field, so an asymmetry is appearing in the distribution of electronic charge, a redistribution of ionic charge it happens, a part of it as localized charge and another one as overlapping charge in the outer cloud region because of the radial deformation of ionic electronic clouds.

The crystalline charge density of diamagnetic ions can be written as a sum of the anionic and cationic charge density, deformed in the radial crystalline field and the unlocalized charge density $\rho^{/A^+/}$ and $\rho^{/B^-/}$ from the overlapping region

$$\rho^{[A^+B^-]}(r) = \rho_{cr}^{[A^+]} + \rho_{cr}^{[B^-]} + \rho_{nl}^{[A^+B^-]} \tag{2}$$

The difference between the electronic density of free ionic system and the electronic charge density of the same ions in crystalline field has the form [10]

$$\Delta\rho^{[A^+B^-]} = \Delta\rho^{[A^+][B^-]} + \rho_{nl}^{[A^+B^-]} \tag{3}$$

and does contain the radial change of the charge density and the change of the charge density because of the putting together of ionic radial deformed ionic clouds.

In a magnetic applied field the outer clouds of the diamagnetic free ions are recessing and the total density current $\vec{j}_{d,f} = \vec{j}_{d,f}^{\,anion} + \vec{j}_{d,f}^{\,cation}$ determining the corresponding magnetic moment, $\vec{M}_{d,f} = \vec{M}_{d,f}^{\,anion} + \vec{M}_{d,f}^{\,cation}$ opposite to the magnetic applied field $\vec{H}$. In crystalline field the magnetic moment is:

$$\vec{M}_{cr} = \vec{M}_{d,cr} + \vec{M}_p = \Delta\vec{M}_{d,cr} + \vec{M}_p \tag{4}$$

where

$$\vec{M}_{d,cr} = \vec{M}_{d,cr}^{anion} + \vec{M}_{d,cr}^{cation} \tag{5}$$

is the diamagnetic moment of ions in crystalline field, $\Delta\vec{M}_{d,cr}$ is determined by the radial deformation of ions and $\vec{M}_p$ corresponds to the induced paramagnetic vortex nanostructure. In order to elucidate the character of the chemical bond in the investigated compounds we have divided the lattice (crystalline) magnetic susceptibility into the Langevin diamagnetic and the Van Vleck paramagnetic terms. In the magnetic field the magnetic susceptibility of diamagnetic ions in crystalline system is given by [8]

$$\chi^{[A^+B^-]} = \chi_{d,cr}{}^{[A^+B^-]} + \chi_p{}^{[A^+B^-]} \tag{6}$$

where

$$\chi_{d,cr}{}^{[A^+,B^-]} = \sum_{\tau=A,B}\{\chi^{\tau}{}_{d,core} + \chi^{\tau}{}_{d,val}\} = \chi_0\left\{\sum_{l=0}^{n-1}\sum_{n=1}^{n_{\max}-1} q_{nl}\left(\overline{r_{nl}^{\,2}}\right)_\tau + \sum_{l=0}^{n_{\max}-1} q_{n_{\max}l}\left(\overline{r_{n_{\max}l}^{\,2}}\right)_\tau g_\tau(r_c)\right\} \tag{7}$$

with $g_\tau(r_c)$ deformation radial functions for diamagnetic ions [7].

The Langevin diamagnetic susceptibility of the ions in the crystalline field can be written in the form

$$\chi_{d,cr}{}^{[A^+,B^-]} = k_i \chi_{d,f}{}^{[A^+][B^-]} \tag{8}$$

k_i being the radial correction coefficient, obtained by use of the anionic and cationic radial correction coefficient in the framework of the deformable ion model [7,8].

The charge redistribution is associated with the change in diamagnetic susceptibility and with emergency of induced Van Vleck paramagnetic susceptibility, such as:

$$\Delta\chi = \chi_{cr}{}^{[A^+B^-]} - \chi_f{}^{[A^+],[B^-]} = \chi_{d,cr}{}^{[A^+,B^-]} + \chi_p{}^{[A^+B^-]} - \chi_{d,f}{}^{[A^+],[B^-]} = \Delta\chi_d{}^{[A^+B^-]} + \chi_p{}^{[A^+B^-]} \tag{9}$$

so it is possible to introduce the effective magnetization coefficients defined as ratio

$$k_{eff} = \frac{\Delta\chi}{\chi_{d,f}} = \frac{\Delta\chi_d{}^{[A^+B^-]} + \chi_p{}^{[A^+B^-]}}{\chi_{d,f}} = \frac{\chi_{d,cr}{}^{[A^+B^-]} - \chi_{d,f}{}^{[A^+][B^-]}}{\chi_{d,f}} + \frac{\chi_p{}^{[A^+B^-]}}{\chi_{d,f}{}^{[A^+][B^-]}} \tag{10}$$

where

$$k_r = \frac{\chi_{d,cr}{}^{[A^+B^-]} - \chi_{d,f}{}^{[A^+][B^-]}}{\chi_{d,f}} = k_i - 1 \tag{11}$$

is radial magnetization coefficient and

$$k_\theta = \frac{\chi_p{}^{[A^+B^-]}}{\chi_{d,f}{}^{[A^+][B^-]}} \tag{12}$$

represents the orbital magnetization coefficient correlated with nonlocalized charge density of ionic system in crystalline field.

The orbital overlapping model of radial deformable ions in crystalline field allows to obtain an available formula for the paramagnetic susceptibility χ_{para} using the diamagnetic susceptibility χ_d [8],

$$\chi_p = \frac{2m}{\hbar^2}(-E_c)\frac{w_{r_0}\cdot\varepsilon_x}{N^*}\frac{a_B^2}{\chi_0}\cdot\chi_{d,cr}^2 = a_p\cdot\chi_{d,cr}^2 \tag{13}$$

where

$$a_p = \frac{2m}{\hbar^2}(-E_c)\cdot\eta_\Gamma\frac{a_B^2}{\chi_0} \tag{14}$$

is orbital magnetic bonding parameter, related with cohesive energy E_c, orbital overlapping parameter η_Γ, strongly related repulsive energy E_R (a_B is Bohr radius and $\chi_0 = \frac{\mathrm{N}e^2\mu_0}{6m_e}a_B^2$ in $m^3/kmol$).

With a little algebra we get the formula for the Van Vleck paramagnetic susceptibility as a function of experimental susceptibility χ

$$\frac{\chi_p/\chi}{(1-\chi_p/\chi)^2} = a_p\chi \tag{15}$$

The ions in the free state present a diamagnetic Langevin susceptibility χ_{dia} calculated in some modes [10]. The action of crystalline potential upon the charge distribution of ions expressed with effective radial coefficient k_i, allows us to express the paramagnetic susceptibility in the form

$$\chi_p = a_p k_i{}^2 \chi_{d,f}{}^2 \tag{16}$$

knowing k_i, a_p and $\chi_{d,f}$, we can determine χ_p. This is a very important fact because there is no other possibility for calculation of the paramagnetic induced susceptibility χ_p, only method to obtain it being to substrate the Langevin susceptibility χ_{dia} from experimental value χ [6, 10]. Using the magnetic coefficients we did obtain from the model of orbital overlapping of radial deformable ions in crystalline field [8,10]

$$\chi_p = a_p\left(\frac{k_i}{k_i + k_0}\right)\chi^2 = a_\chi\chi^2 \tag{17}$$

3. Results and discussions

Using the magnetic susceptibility experimental data χ [5,6], the calculated values χ_{dia} [7, 8, 10], and the effective radial correction coefficient k_i [7], were obtained the magnetization coefficients, radial k_r and orbital k_o as they were defined in the framework of the model presented. For alkali halides it is observed in fig.1 that the ionic distortion largely differs from anion to cation. The anions are tightening and the cations are loosening in crystal relative to free state. When the positive ion size largely differs from there negative partner in crystalline state (LiBr, NaBr), the ionic distortion of the cation is negligible relative to that of the anion, the second neighbour repulsion becoming predominant. Thus, the orbital overlapping is determined only by negative ions, so the big part from k_i being given by them.

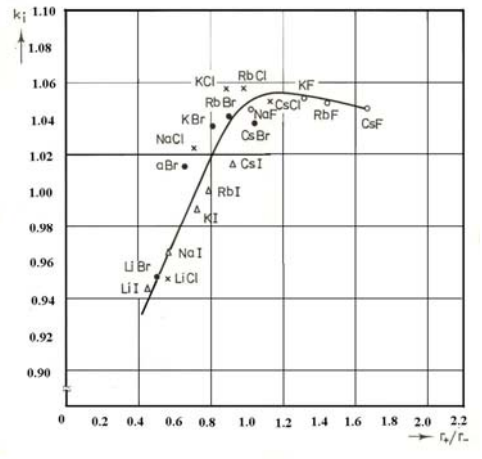

Fig. 1. Effective radial correction coefficient for alkali halide.

A comparative analysis of the effective coefficient k_{eff} shows that in ionic crystalline compounds like alkali halides, small values of k_{eff} are corresponding to a magnetic susceptibility χ in the crystal comparable with that of the ions in the free state, χ_f. So, the susceptibility of the crystalline system can be considered as a sum of the susceptibilities of free ions, but radial k_r and orbital k_o, coefficients being different from zero, allows us to suppose that the radial and orbital deformation of ions does exist in a very strong relationship with the change in Langevin susceptibility $\Delta\chi_{d,cr}$ on a part and the emergence of Van Vleck susceptibility χ_{para} on the other part.

These entities can be equals when the corresponding diamagnetic and paramagnetic moments are opposite and have the same values. When one of the ions from the crystalline system is much smaller then its partner, the overlap of the outer clouds becomes very important. For lithium halides, because Li^+ ion is too small then its negative partner, the ionic system has a diamagnetic susceptibility smaller then that of the same ionic system in the free state.

The contribution of the radial deformation is given by the amount $\Delta\chi = \left|\chi_{d,cr} - \chi_{d,f}\right|$, which is increasing from LiF to LiI. A very important increasing of the diamagnetic susceptibilities is observed when the ions are passing from free state in crystalline state for systems compose by ions (anion and cation) with an isoelectronic structure like NaF, KCl, RbBr (fig.1), where the interaction of the different kind of ions becomes more important then that of the interaction of ions from the second coordination sphere [11]. It is very clear that nanostructures originated in radial deformation of ionic outer clouds and in the emergence of the induced Van Vleck paramagnetic quantum vortex can explain the magnetic behaviour of the ionic-covalent (and covalent-ionic) crystalline systems, for alkali halides in this case.

4. Conclusions

The model and the method introduced in this paper in an original way, allow us to evaluate the magnetic behaviour of the ionic-covalent compounds like alkali halides as nanostructural changes and to calculate the diamagnetic and paramagnetic susceptibilities. The calculation of the absolute value of ratio $\chi_{para}/\chi_{dia}, \approx 0.11$ for isoelectronic structures in alkali halides (NaF, KCl, RbBr) in the framework of the model introduced show that these compounds are strongly ionic. We suppose that our model is a very important instrument in the study of others ionic-covalent compounds like alkali earth oxides, ammonium halides, where like in alkali halides, the radial deformation and the induced paramagnetic vortex nanostructures are responsible for magnetic changes in these systems.

References

[1] J. H. Van Vleck, The theory of electric and magnetic susceptibilities, Oxford Univ. Press, Oxford (1932).
[2] R. Smytkowsky, Phys.Rev. **65**, 032112 (2002).
[3] T. K. Rebane, Vestn, Len. Univ. **22**, 20 (1965).
[4] Ts. Z. Vitkina, L. K. Orlik, N. S. Orlova, O. E. Andreeva, Cryst. Rest. Technol **35**, 2, 229 (2000).
[5] P. Selwood, Magnetochemistry, New York, (1943).
[6] Ya. G, Dorfman.Diamagnetismi khimicheskaya svyaz, Fizmatgiz, Moskow (1961).
[7] I. G. Pop, Studia UBB, Cluj-Napoca, Physica XXX, 61 (1985).
[8] I. G. Pop, Thesis: Magnetic properties of ions, Univ Babes-Bolyai, Cluj (1987).
[9] R. F. W. Bader, The Force Concept in Chemistry, Van Nostrand Reinhold, NewYork (1980).
[10] I. G. Pop, Magnetic properties of ions, Risoprint, Cluj-Napoca (2005).
[11] S. C. Agrawal, Indian J. Phys. **55A**, 385 (1981).

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