NMR in Van Vleck magnetics and intermolecular interactions in molecular crystals and Chevrel phases

S P Gabuda, S G Kozlova, A G Lundin

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<u>Abstract.</u> Aspects of orbital paramagnetism and intermolecular interactions are discussed in relation to compounds containing octahedral MF_6 molecules (where M ia a transition metal) and Chevrel phase cuboctahedron systems M_6X_8 . The 100th anniversary of the birth of Professor S A Altshuler, a pioneer in the use of NMR for studying Van Vleck magnetism, is a motivation for this review.

S P Gabuda, S G Kozlova Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrent'eva 3, 630090 Novosibirsk, Russian Federation Tel. (7-393) 330 75 31. Fax (7-393) 330 94 89 E-mail: gabuda@niic.nsc.ru, sgk@niic.nsc.ru A G Lundin Siberian State Technological University, prosp. Mira 82, 660049 Krasnoyarsk, Russian Federation Tel. (7-391) 227 39 25. Fax (7-391) 227 23 73 E-mail: arlund@rol.ru

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1. Introduction

Van Vleck, or temperature-independent, paramagnetism is associated with the presence of ions of transition and rareearth (RE) elements with an even number of electrons in the partly filled d and f shells [1, 2]. Such systems can be characterized by a singlet ground state and by a zero magnetic moment, and the degeneracy of their state cannot be lifted by the action of a crystal field or by the accompanying mixing of orbitals. But in the presence of a magnetic moment at the nuclei of such ions, the ψ_j^0 orbitals of the ground state become perturbed and various $\lambda \psi_k^0$ excited states are admixed with ψ_j^0 . As a result of this perturbation, the ion acquires an 'induced' magnetic moment, and the substances that contain Van Vleck ions have a temperature-independent paramagnetic susceptibility [1].

The theoretical analysis of the possibility of observing nuclear magnetic resonance (NMR) in similar systems and the studies of its features and of the information that can be obtained from these studies were started in Kazan in 1956 [3]. Experimentally, the magnetic resonance in a Van Vleck magnetic was first revealed for impurity V^{3+} ions (with the electron configuration $3d^2$) in corundum (Al₂O₃) [2]. Later,

detailed investigations of NMR in a number of crystalline compounds of RE elements with an even number of f shell electrons were performed; the results of these studies can be found in reviews [4–6]. One of these results was the conclusion that the Van Vleck ions, such as Tm^{3+} , do not exert a significant effect on the NMR of the nuclei of the diamagnetic ions ¹⁹F (in LiTmF₄) and ¹H (in the hydrate of the thulium ethyl sulfate) [4, 5].

However, it was revealed that this approach cannot be extended to the Van Vleck paramagnets of transition-metal compounds. In particular, the parameters of the ¹⁹F NMR spectra of the molecular crystal PtF₆, in which the central ion Pt^{6+} has the electron configuration $5d^4$, correspond to the parameters of Van Vleck ions [7], although formally the [F]⁻ ions are not Van Vleck ions. Analogous conclusions were obtained for the ionic crystals K₂RuF₆, K₂OsF₆, and KIrF₆, which have a strong temperature-independent paramagnetism and the electron configurations 4d⁴ and 5d⁴ of the central ions [8, 9]. These results indicate that in this case, the mixed wave functions of the ground (ψ_i^0) and excited $(\lambda \psi_k^0)$ states pertain to the molecular orbitals of molecules and molecular ions, rather than to individual ions, and that the 'induced' magnetic moments are induced to one extent or another in all atoms of such systems.

The mixed character of the ground state of molecules that have temperature-independent paramagnetism can be one of the main reasons for the substantial difference in their intermolecular interactions from the interactions between isostructural diamagnetic molecules. It is known, in particular, that the pressure of saturated vapors over the surface of solid PtF_6 is an order-of-magnitude lower than that over the diamagnetic WF_6 [10], whose molecular and crystal structure parameters are virtually identical to the parameters of solid PtF_6 . This means that the Van Vleck paramagnetism of PtF_6 leads to an increase in the cohesion forces between the molecules and in the intermolecular interaction compared to the diamagnetic WF₆. The same character of the relation between the forces of intermolecular interaction follows from an approximately 20% increase in the melting and boiling temperatures of PtF₆ relative to the melting and boiling temperatures of WF₆ [11].

The parameters of NMR spectra characteristic of Van Vleck magnetics are also observed in the nuclei of diamagnetic ligands X^{2-} (³³S, ⁷⁷Se, ¹²⁵Te, etc.) of more complex cuboctahedral molecules and molecular ions M_6X_8 [12, 13]. In these compounds, the ions of transition metals M (with the electron configurations nd^2 and nd^4) are located at the centers of the faces, and the X atoms are in the centers of the cuboctahedra.

Of special interest are dimeric groups $\{[M_6X_7]C[M_6X_7]\}$, in which the cuboctahedral subunits are connected through a common vertex, a carbon C⁴⁺ ion. According to the data on the NMR of ¹³C [14, 15], the change in the oxidation state of such a dimeric group is accompanied by an anomalous change in spectra, which indicates the switching-on and switching-off of metal-metal bonds between two subunits, the metal cluster $[M_6X_7]$ groups. Such a system can be interesting as a promising model of a single-molecule switching key ('nanotransistor') with a variable oxidation state [16]. We also note that many representatives of this class of compounds, for example, so-called Chevrel phases (CPs) (e.g., Mo₆X₈), have metallic properties and low-temperature superconductivity [17, 18] and the ternary compound PbMo₆S₈ in the superconducting state (at temperatures below ≈ 15 K) has record high values of the density of critical current and magnetic fields reaching ~ 100 T [19, 20].

The detailed investigations of the macroscopic properties performed in [17, 18] did not lead to a clarification of the mechanism of the interrelation between the extremely high values of critical magnetic fields and the cluster structure of CP compounds. At the same time, NMR studies of these compounds [19–27] revealed a strong inhomogeneity of the distribution of local magnetic fields in the nuclei of the ²⁰⁷Pb, ¹¹⁷Sn, ¹¹⁹Sn, ⁹⁵Mo, ³³S, and ⁷⁷Se ions. It turned out that the Knight shifts in the ³³S and ⁷⁷Se nuclei are one to two orders of magnitude less than those at the nuclei of metallic atoms, and that the Knight shift even reverses sign for the ³³S nuclei. At the same time, according to the data on NMR relaxation, the s and p electrons of S, Se, Pb, and Sn take part in superconductivity along with the 4d electrons of Mo.

Later, it was established in the example of isoelectronic metal clusters [Re₆Te₈] [13] that the inhomogeneity of the distribution of local magnetic fields in such systems can be related to the peculiarities of Van Vleck paramagnetism and to the symmetry of molecular orbitals in cuboctahedral groups like [M_6X_8]. Because of the specific features of the symmetry of the highest occupied orbitals, the direction of the circulation of orbital currents in the anions is opposite to the direction of circulation of currents in Re atoms. As a result, the external magnetic field becomes higher in the region of the location of M cations and is weakened near the X anions located at the corners of the [M_6X_8] cuboctahedra.

In this review, we detail the physical mechanisms of the appearance of counter circulation of intramolecular orbital currents and related inhomogeneities of local magnetic fields, the character of intermolecular interactions, and their effect on the microscopic and macroscopic properties of some Van Vleck magnetics.

2. Basic principles

The Van Vleck paramagnetism is a second-order perturbation theory effect of the terms in the spin Hamiltonian that are linear in the external magnetic field *H*. In terms of the crystal field theory, the magnetic susceptibility χ_{VV} of a Van Vleck magnetic is written as [1]

$$\chi_{\rm VV} = 2(g_J \mu_{\rm B})^2 \sum_n (E_n - E_0)^{-1} |\langle 0|J|n \rangle|^2, \qquad (1)$$

where E_n and $|n\rangle$ denote the energy and the wave function of the *n*th state of the ion in a crystal field and 0 refers to the ground singlet state. The difference $E_n - E_0$ corresponds to a change in the energy upon a single-electron excitation $0 \rightarrow n$, J is the total angular momentum of the ion, equal to the sum of the orbital (L) and spin (S) momenta, μ_B is the Bohr magneton, and g_J is the spectroscopic splitting factor (Landé factor) [1].

The applied magnetic field *H* polarizes the electron shell of the Van Vleck ion, induces the magnetic dipole moment $\mu_{ion} = \chi_{VV} \mathbf{H}$, and enhances the magnetic field at the location of the nucleus of a given ion in the crystal. The induced electron magnetic moments of Van Vleck ions μ_{ion} are identical both in magnitude and in direction. This constitutes the main difference between Van Vleck magnetics and ordinary paramagnets (obeying the Curie–Weiss law), in which the magnetic moments of ions are in degenerate states, resulting in an inhomogeneous broadening of the NMR spectra.

Compound	HoVO ₄	TmSb	PrAlO ₃	$(\mathrm{Al}_x, \mathrm{V}_{1-x})_2\mathrm{O}_3$	LiT	mF ₄
Nucleus	¹⁶⁵ Ho	¹⁶⁹ Tm	¹⁴¹ Pr	51 V	¹⁶⁹ Tm	¹⁹ F
Ion (electron configuration)	$Ho^{3+} (4f^{10})$	$Tm^{3+}\;(4f^{12})$	$Pr^{3+} (4f^2)$	$V^{3+} (3d^2)$	$Tm^{3+} \ (4f^{12})$	$F^{-}\left(2p^{6} ight)$
$-\sigma_x$	175 ± 5	88.7	0.539 ± 0.02	2.70 ± 0.03	68.9	-7.8 %
$-\sigma_y$	175 ± 5	88.7	0.539 ± 0.02	2.70 ± 0.03	68.9	-2.0 %
$-\sigma_z$	~ 0	88.7	6.18 ± 0.50	~ 0	1.765	9.8 %
$-\sigma_{ m isotr}$	117	88.7	2.42	~ 1.8	48.5	~ 0

Table 1. Components of the tensors of magnetic shielding σ_i of the nuclei of Van Vleck ions in some crystals of RE compounds [1]. T = 4.2 K.

An increase in the magnetic field leads to a shift of the NMR absorption frequency v of the nuclei of Van Vleck ions toward higher values relative to the Larmor frequency v_L of the NMR of the nucleus (in the unaltered external magnetic field **H**₀). The relative shift $\sigma = (v_L - v)/v_L$ of the observed frequency of the NMR absorption is proportional to the magnetic susceptibility χ_{VV} and to the hyperfine electron–nucleus coupling constant *A* [1]:

$$\sigma = -\frac{A\chi_{\rm VV}}{g_J \mu_{\rm B} \gamma \hbar} = -2A \frac{g_J \mu_{\rm B}}{\gamma \hbar} \sum_n (E_n - E_0)^{-1} \left| \left\langle 0 | J | n \right\rangle \right|^2.$$
(2)

The parameter σ , or the constant of magnetic shielding of the nucleus, is generally a second-rank tensor [29, 30], whose components are determined by the concrete structure of the crystal. The negative sign of the constant agrees with the notation adopted in computational methods of the density functional theory (DFT), which are realized in a number of program packages, such as GAUSSIAN [32] and ADF (Amsterdam Density Functional) [33].

2.1 Van Vleck magnetics of RE compounds

At normal temperatures, the magnetic susceptibility of RE compounds containing ions with an even number of electrons in the f shells [Pr³⁺ (4f²), Ho³⁺ (4f¹⁰), Tm³⁺ (4f¹²), etc.] usually obey the Curie–Weiss law. But at low temperatures, substantial deviations from this law are frequently observed in such compounds and the magnetic susceptibility of RE compounds becomes temperature independent. This is because the ground state of these systems is a singlet, separated from the excited Stark sublevels of RE ions by small energy gaps $\Delta E = E_1 - E_0 \approx 10 \text{ cm}^{-1}$ [1].

More information on the properties of Van Vleck magnetics of RE compounds can be obtained using magnetic resonance methods [1]. The results of detailed low-temperature investigations of Van Vleck ions in a number of RE compounds are presented in reviews [4–6]. In particular, the parameters σ of the magnetic shielding tensors of the nuclei of Van Vleck ions have been found; their typical values are given in Table 1.

We note the extremely large ('giant' [1]) values of the components of the magnetic shielding tensor σ , which apparently are due to the above-mentioned small splitting ΔE of the Stark sublevels of the RE ions. The large values of σ correspond to a manyfold increase (up to two orders of magnitude) in the frequency v of the magnetic resonance of Van Vleck ions relative to the Larmor frequency v_L of their free nuclei. Because the frequency of the magnetic spin resonance is proportional to the magnetic field strength, the signal of the magnetic resonance of Van Vleck ions at the frequency $v_L = \gamma G_0$ is shifted toward lower fields, $H_{\text{res}} = H_0/(1 - \sigma)$. Therefore, the negative values of the magnetic shielding constant σ for the nuclei of Van Vleck ions

correspond to negative values of the magnetic resonance shift $\Delta H = H_{res} - H_0 = \sigma H_{res}$.

The results of the study of NMR spectra of the ¹⁹F nuclei of nonmagnetic F⁻ ions in the fluorides and of ¹H nuclei in H₂O molecules in crystal hydrates of compounds containing Van Vleck RE ions are presented in [4, 5, 34–37]. It has been established that the magnetic moments of Van Vleck ions exert virtually no effect on the width and shape of the NMR lines of ¹⁹F ions (just like ¹H ions in crystal hydrates of RE compounds), and their NMR spectra are almost identical to those observed in diamagnetic crystals [1, 4, 5].

As an example, we consider data of a low-temperature investigation of the double lithium-thulium fluoride crystal LiTmF₄ in the range of the NMR frequencies of 19 F [36]. The last column in Table 1 gives values of the components of the magnetic shielding tensor of ¹⁹F nuclei obtained at the temperature 4.2 K. The z axis of the tensor is oriented along the Tm-F bond. The observed value of the longitudinal component $\sigma_z = -9.8\%$ of the ¹⁹F shielding tensor is due to the direct contribution from the local magnetic field $H_{\rm loc} =$ $\mu R^{-3}(3\cos^2\theta - 1)$ of the Van Vleck ion Tm³⁺, whose dipole moment is $\mu_{ion} = \chi_{VV} \mathbf{H}$ and where *R* is the Tm-F spacing and θ is the angle between the vector **R**(Tm-F) and the magnetic field H. If the magnetic field is oriented along the Tm-F bond, this field is added to the external magnetic field H_0 , which allows observing the signal of the ¹⁹F nuclei at smaller values (by 9.8%) of the applied magnetic field $H = H_0 + H_{loc}$. The shielding tensor is strongly nonaxial and its transverse components σ_x and σ_y correspond to a shift of the ¹⁹F NMR signals toward larger values (from 2 to 7.8%) of the applied magnetic field $H = H_0 + H_{loc}$. The isotropic component of the shielding, $\sigma_{\rm isotr}$, for the ¹⁹F nuclei is close to zero, which indicates a purely dipole mechanism of magnetic shielding of the ¹⁹F nuclei in LiTmF₄.

The above features are apparently related to only a weak overlap of the f orbitals of the Van Vleck RE ions with the wave functions of the ligands. But for the compounds of transition metals containing Van Vleck ions with an even number of electrons in their partly filled d shells, the appearance of the effects of electron delocalization and transfer of the spin density of induced magnetic moments of d ions to the ions of nonmagnetic ligands can be expected, because the d electrons of the ions of transition elements are less shielded than the f electrons.

2.2 Magnetic shielding of ¹⁹F nuclei in molecules and complexes of transition metals with partly filled d shells (d², d⁴, and d⁶)

In octahedral molecules and molecular $[MF_6]^{x-}$ ions (x = 0, 1, 2, 3), the crystal field with the O_h symmetry splits the d level of the central $[M]^{(6-x)+}$ ion into a doublet e_g and a triplet t_{2g};

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Compound	Configuration	χ , cm ³ mol ⁻¹	$\Delta E, \mathrm{cm}^{-1}*$	$-\sigma_{\parallel}, \mathrm{ppm}$	$-\sigma_{\perp}, \text{ppm}$	$-\sigma_{isotr}$, ppm	A _s , MHz	$f_{\rm s}, \%$				
$OsF_6 (T < 115 \text{ K})$	5d ²	_	1112.6	13700	7700	9700						
PtF ₆ ¹⁹ F				6900	3700	4800 ± 60	263.6	0.585				
PtF ₆ ¹⁹⁵ Pt	5d ⁴	812	3992.4	$\sigma_{\rm isotr} (^{195}{\rm Pt}) = -4521.3 \; \rm ppm^*$								
K[IrF ₆]	5d ⁴	784 ± 7	4887.7	3360	1900	2390	155.7	0.346				
$K_2[OsF_6]$	5d ⁴	659 ± 5	5113.5	1880	1240	1560	129.4	0.287				
$K_2[RuF_6]$	$4d^4$	4250 ± 40	1564.7	9820	5300	6810	73.2	0.163				
$K_2[NiF_6]$	3d ⁶	—	14260	210 ± 20	-200 ± 20	-60 ± 20	_	_				
$K_2[PdF_6]$	4d ⁶	_	17172	180 ± 20	-180 ± 20	-60 ± 20	_	_				
$K_3[RhF_6]$	4d ⁶	_	14349	100 ± 5	-422 ± 5	-250 ± 5	_	_				
$K_2[PtF_6]$	5d ⁶	_	20874	160 ± 20	-230 ± 20	-100 ± 20	—	_				
* Data from [40]; pp	* Data from [40]; ppm = part per million.											

Table 2. Parameters of magnetic shielding tensors of ¹⁹F nuclei in molecular hexafluorides and hexafluorine complexes of Van Vleck ions with partly occupied d shells [39].

the latter, because of the spin–orbit interaction, is additionally split into a doublet $U_{3/2g}$ and a singlet $E_{5/2g}$. For the d⁴ electron configuration of the central ion, the $U_{3/2g}$ level is the highest occupied and nondegenerate state, and the singlet $E_{5/2g}$ is the lowest unoccupied level. These states can mix under the effect of a magnetic field, which causes the temperature-independent paramagnetism of compounds of this type, characteristic of Van Vleck magnetics. As was established experimentally, the magnetic properties of the platinum hexafluoride PtF₆, isoelectronic molecular compounds IrF₅, RhF₅ [38], and complex compounds KIrF₆, K₂OsF₆, and K₂RuF₆ (Table 2) indeed demonstrate temperature-independent paramagnetism, and the range of stability of this state ranges up to room temperature and even higher temperatures [7, 8, 38, 39, 41–44].

The values of the ΔE splitting between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of free molecules and $[MF_6]^{x-}$ anions (see Table 2) were calculated in terms of the DFT using the ADF-2008-02 program package [32, 33] with the scalar relativistic corrections and the contribution from spin-orbit interactions taken into account. The values of ΔE obtained for the d elements are several tens or even hundreds of times higher than the corresponding values of the ΔE splitting for the RE ions. For this reason, the region of the existence of a temperature-independent state of magnetic susceptibility reaches temperatures exceeding room temperature, and the induced magnetic moments of Van Vleck ions of d elements and the average values of the isotropic components of the magnetic shielding of σ_{isotr} nuclei are substantially less than the corresponding values for Van Vleck f ions.

Table 2 contains the experimental values of σ_{isotr} and of the components of the magnetic shielding tensor of ¹⁹F nuclei in molecular hexafluorides and isoelectronic complexes of transition-metal ions with partly occupied d shells (d², d⁴, and d⁶) [7–9, 38, 41–44]. We note that σ_{isotr} , or the coefficient of the magnetic field enhancement at the locations of the nuclei of nonmagnetic F⁻ ligands in $[MF_6]^{x-}$ complexes with the d² and d⁴ electron configurations of the central ions, reaches values of a few fractions of a percent (or several thousand ppm) of the applied magnetic field.

These values are an order of magnitude less than the data given in Table 1 for the σ_i components of the ¹⁹F

nuclei in the structure of LiTmF₄. However, for compounds of the transition metals under consideration, the values of the isotropic components of shielding are nonzero, $\sigma_{isotr} ({}^{19}F) \neq 0$, in contrast to those for LiTmF₄. This means that the mechanism of shielding of the ${}^{19}F$ nuclei in transition-metal compounds is not purely dipole, and the isotropic σ_{isotr} components correspond to 'induced' magnetic moments of F⁻ ions in Van Vleck molecules and complex transition-metal fluorides.

The mechanism of the appearance of 'induced' magnetic moments in F⁻ ions characterized by a closed 8-electron shell is a consequence of the overlap of the wave functions of 2s electrons of the F⁻ ions with the wave functions of the d electrons of the transition metal ions. Using formula (2) and experimental values of the magnetic susceptibilities χ and magnetic shielding constants σ_{isotr} , we calculated the constants of the hyperfine electron-nucleus interaction A of the ¹⁹F nuclei. The values of the constant A thus found allow calculating the coefficients $f_s = A_s/A_s[F^0]$, where $A_s[F^0] =$ 4.51×10^{10} Hz is the tabulated value of the hyperfine interaction constant of the ¹⁹F nucleus with the unpaired 2s electron in the free atom of fluorine [8, 39, 45]. The calculated f_s coefficients characterize the magnitudes of the induced spin density of 2s electrons in the nuclei of F⁻ ions in the crystals under consideration.

The values of the parameters obtained indicate that the nonmagnetic F^- ions in the crystals of compounds of transition metals with partly occupied d shells can be characterized by induced magnetic moments and by the related hyperfine interaction constants. This means that in the systems under consideration, the contributions from the overlap of d orbitals with the wave functions of the ligands are quite substantial, and the functions $|n\rangle$ in formulas (1) and (2) are combinations of the wave functions of the *n*th states of the d ions and the wave functions of the diamagnetic ligands, with the coefficients f_s characterizing the contribution of the orbitals of the fluorine atoms to the total molecular orbital of the system.

2.3 Anisotropy of magnetic shielding

Another consequence of the overlap of the wave functions of 2s electrons of F^- ions with the wave functions of d electrons of transition-metal ions is the appearance of a strong anisotropy of magnetic shielding of the nuclei of nonmag-

netic ligands. The principal mechanism of this phenomenon is related to the effect of hybridization of the 2s and 2p orbitals of F^- ions; because of this effect, the appearance of an induced spin density of 2s electrons in the ¹⁹F nuclei is accompanied by the transfer of spin density to the $2p_{\sigma}$ orbitals that are 'frozen' in the M-F bonds. Therefore, the hyperfine coupling constant of ¹⁹F nuclei in the general case is represented as

$$A = A_{\rm s} + (A_{\rm p\sigma} - A_{\rm p\pi})(3\cos^2\theta - 1), \qquad (3)$$

where θ is the angle between the orientation of the M-F bond and the direction of the magnetic field. The isotropic term A_s is determined by the transfer of spin density to the 2s states; the second term is determined by the anisotropic hyperfine interaction, which is due to the transfer of the electron spin to the states with a nonzero orbital moment in the σ and π orbitals. The 'induced' magnetic moments $\mu_{ion} = \chi_{VV} H$ of the central ions thus create local magnetic fields H_{loc} in the region of localization of ¹⁹F nuclei; the corresponding shielding constant is written as

$$\sigma = -\frac{A\chi_{\rm v-V}}{g_J\mu_{\rm B}\gamma\hbar} = -\frac{\left[A_{\rm s} + (A_{\rm p\sigma} - A_{\rm p\pi})(3\cos^2\theta - 1)\right]\chi_{\rm v-V}}{g_J\mu_{\rm B}\gamma\hbar}.$$
 (4)

Usually, the component related to the electron spin transfer to the $2p_{\sigma}$ orbitals prevails; therefore, as a rule, $A_{p\sigma} > A_{p\pi}$. At $\theta = 0$, the contribution from the anisotropic component of shielding leads to an increase in H_{loc} and to a shift of the magnetic resonance signal of F^- ions (at the frequency $v_{\rm L} = \gamma H_0$) toward lower fields, $H_{\rm res\,\parallel} = H_0/(1 - \sigma_{\parallel})$. At $\theta = 90^\circ$, the contribution of the anisotropic component of shielding leads to a decrease in $H_{\rm loc}$ and a shift of the magnetic resonance signal of F^- ions toward higher magnetic fields, $H_{\rm res\,\perp} = H_0/(1 - \sigma_{\perp})$.

In the case of polycrystalline samples with an isotropic orientation of the M-F bonds, the ¹⁹F NMR signals of individual crystallites composing the crystal refer to the region of magnetic fields from $H_{\text{res}\parallel}$ to $H_{\text{res}\perp}$, and the shape of the spectrum envelope describes the distribution of the relative number of crystallites with the orientation of the M-F bonds in an angular range $(\theta, \theta + d\theta)$. The exact shape of such an envelope corresponds to systems with a uniaxial anisotropy of the magnetic shielding tensor of the nuclei [46].

Figure 1 displays the ¹⁹F NMR spectra of polycrystals of some Van Vleck magnetics, namely, of molecular hexafluorides and isoelectronic complexes of transition-metal ions with partly filled d^2 , d^4 , and d^6 shells [7–9, 38, 41–44].

For the ¹⁹F nuclei in such crystals, the experimental values of the longitudinal (σ_{\parallel}) and transverse (σ_{\perp}) components of the magnetic shielding tensors (relative to the orientation of the *M*-F bonds), are given in Table 2. The most important result is the correlation revealed between the values of the isotropic component of shielding σ_{isotr} and the anisotropy of shielding $\Delta \sigma = \sigma_{\perp} - \sigma_{\parallel}$, depending on the number of d electrons at the central ion (Fig. 2). Such a correlation can be a direct consequence of the constancy of the hybridization parameters of 2s and 2p orbitals of the F⁻ ions in a number of octahedral molecules and of the related constancy of the relation between the coefficients of transfer of spin density from the Van Vleck ions onto the 2s and 2p orbitals of the 'nonmagnetic' F⁻ anions.

At the same time, a deviation from this correlation can be noted for the octahedral complexes of transition metals with



Figure 1. Absorption NMR spectra of ¹⁹F in polycrystals of Van Vleck magnets OsF₆, PtF₆, and K₂PtF₈. Positions of the longitudinal (σ_{\parallel}) and transverse (σ_{\perp}) components of the asymmetric spectra are shown. The position of the origin of the σ scale corresponds to the value for the idealized [F]⁻ ion.



Figure 2. Correlation diagram of the dependence of the anisotropy $\Delta \sigma = \sigma_{\perp} - \sigma_{\parallel}$ on σ_{isotr} for the tensors of magnetic shielding of ¹⁹F nuclei in octahedral molecules and MF_6 ions.

partly filled d⁶ shells (see Figs 1 and 2). For these complexes, the sublevels $U_{3/2g}$ and $E_{5/2g}$ of the triplet HOMO state t_{2g} are occupied, and the LUMO state e_g is separated from the ground state by a gap approximately equal to 15,000–20,000 cm⁻¹ (see Table 2). This means that the induced magnetic moments of the Pt⁴⁺, Ni⁴⁺, Pd⁴⁺, and Rh³⁺ ions with the electron configurations d⁶ are small and, consequently, the values of σ_{isotr} and $\Delta\sigma$ should also be small. The observed deviation from the linear dependence $\Delta\sigma(\sigma_{isotr})$ can indicate the existence of some unexpected mechanisms of nuclear shielding, whose contributions are substantial in the case of very small values of the induced magnetic moments in Van Vleck ions.

2.4 Comparison of the magnetic shielding of ¹⁹F nuclei in octahedral complexes of transition metals with partly filled d⁶ shells

and in diamagnetic hexafluorides

A feature related to the change of the sign of σ_{isotr} for the complexes of transition metals with the d⁶ electron configurations of ions remains unexplained. We note that the positive sign of σ_{isotr} corresponds to a weakening of the local

Compound	$\Delta E,$ cm ⁻¹ *	$cm^3 mol^{-1}$	$-\sigma_{\parallel}, { m ppm}$	$-\sigma_{\perp}$, ppm	$-\sigma_{\rm isotr}$, ppm					
MoF ₆ (4p ⁶)	31891	-26	245	530	430 ± 20					
TeF ₆ (4d ¹⁰)	34617	-66	133	350	277 ± 6					
$WF_{6}(4f^{14})$	39483	-53	230	440	370 ± 20					
$K_2[TiF_6](3p^6)$	38989	—	162 ± 15	484 ± 15	377 ± 25					
$K_2[ZrF_6](4p^6)$	45264	—	$\sim 0\pm 20$	420 ± 20	280 ± 20					
$Cs_2[SnF_6]$ (4d ¹⁰)	45312		95 ± 10	180 ± 10	150 ± 10					
* Results of DFT calculations for free molecules and molecular ions with scalar relativistic corrections and spin-orbit interaction taken into account.										

Table 3. Experimental values of the principal components of the magnetic shielding tensors of ¹⁹F nuclei in diamagnetic hexafluorides and hexafluorine complexes of some transition metals.

magnetic field, which introduces a certain contribution to the diamagnetic component of the magnetic susceptibility of the system. At the same time, as can be seen from Fig. 1, the shape of the ¹⁹F NMR spectrum of the polycrystalline K₂PtF₆ with the $5d^6$ electron configuration of the central Pt^{4+} ion completely corresponds to the shape of the NMR spectra of Van Vleck paramagnets with the d⁴ and d² configurations of the central ions. In terms of the model of Van Vleck magnetism, this can mean that in the case of the d⁶ configuration of central ions, the 'induced' magnetic moments of these ions change sign, which leads to the appearance of induced diamagnetism, or the 'demagnetization' of the fluorine ions in such systems. An alternative assumption is that the sign reversal occurs only for the induced magnetic moments of diamagnetic F⁻ ions, in which case the magnetic susceptibility of the system on the whole corresponds to weak paramagnetism.

A comparison of the ¹⁹F NMR spectra of diamagnetic hexafluorides containing transition-metal ions with unoccupied d⁰ shells (or with the completely occupied d¹⁰ and f¹⁴ shells) with the spectra of complexes of transition metals with d⁶ electron configurations (Fig. 3) supports the abovementioned alternative assumption. In both cases, the longitudinal (σ_{\parallel}) components of the magnetic shielding tensors of the ¹⁹F nuclei are virtually coincident. Consequently, the effects of 'induced' magnetic moments of central ions are virtually absent in both cases. The diamagnets exhibit a shift of the transverse components σ_{\perp} toward weaker magnetic fields, i.e., an increase in the magnetic field in the ¹⁹F nuclei when the field orientation is perpendicular to the *M*–F bonds. Because the opposite effect—a shift of σ_{\perp} toward



Figure 3. Comparison of the NMR spectra of ¹⁹F in (a) octahedral molecules with unoccupied d⁰ shells and closed d¹⁰ and f¹⁴ shells, and (b) complexes with partly occupied d⁶ shells of central ions. $T \approx 77$ K, $v_L = 200$ MHz.

stronger fields — is observed for those complexes with the d^6 electron configuration of the ions of transition metals, it should be assumed that this occurs as a result of the action of an additional, molecular mechanism of 'demagnetization,' or a weakening of the magnetic field at the ¹⁹F nuclei.

Table 3 gives experimental values of the components of the magnetic shielding tensor of ¹⁹F nuclei in diamagnets, such as K₂[TiF₆] isostructural to K₂[PtF₆], and diamagnetic molecular hexafluorides MoF₆, WF₆, and TeF₆, which have closed p⁶, d¹⁰, and f¹⁴ shells [7, 39, 41–44]. It follows from a comparison with the data in Table 2 that the 'mirror-like' character of the relation between the transverse (σ_{\perp}) and longitudinal (σ_{\parallel}) components of the shielding tensors of the ¹⁹F nuclei in diamagnets is a common rule. The microscopic mechanism of the appearance of this phenomenon is discussed in Section 3.

3. Antibonding d electrons and the orbital component of the Van Vleck paramagnetism

By antibonding electrons, we mean those electrons that occupy the so-called molecular antibinding orbitals, which are characterized by the presence of nodes and by the change of sign upon transition from one atom to another. A wellknown fact is the effect of antibonding 2p electrons on the structure of O_2 and F_2 molecules, which leads to a large decrease in the binding energy U and to a noticeable increase in the bond length in the sequence $N_2 \rightarrow O_2 \rightarrow F_2$. It can be noted that the d electrons of transition-metal ions in compounds with coordination bonds always occupy the antibinding orbitals of the molecules and molecular ions, but the specific features of their influence on magnetic shielding, the structure of molecules, and interactions in such compounds remain insufficiently systematized to date.

3.1 Orbital contribution

to the paramagnetic component of shielding

The appearance of induced magnetic moments in F^- ions involved in the composition of octahedral MF_6 molecules and molecular $[MF_6]^{n-}$ ions is generally ascribed to the effect of the overlap of the orbitals of the *M* and F atoms, which results in a partial dequenching of the orbital moments of p and d electrons [29]. In perturbation theory terms, the wave functions of molecular ions similar to the octahedral $[MF_6]^{n-}$ groups are represented as linear combinations of the initial (unperturbed) wave functions. The external magnetic field oriented parallel to the direction of the M-Fbond cannot perturb the axial symmetry of such a system.

Symmetry	Orbitals ¹ of the central ion	Linear combinations of p_σ and p_π orbitals of ligands 2	Population in the ground state
e _g *	$\frac{(1-a^2)^{1/2} d_{x^2-y^2}}{(1-a^2)^{1/2} d_{z^2}}$	$+a\{(1/2)(\sigma_2 + \sigma_5 - \sigma_3 - \sigma_6)\} \\+a\{(1/\sqrt{12})(2\sigma_1 + 2\sigma_4 - \sigma_2 - \sigma_5 - \sigma_6 - \sigma_3)\}$	Unoccupied "
t [*] _{2g}	$egin{array}{l} (1-b^2)^{1/2}\mathrm{d}_{xy}\ (1-b^2)^{1/2}\mathrm{d}_{xz}\ (1-b^2)^{1/2}\mathrm{d}_{yz} \end{array}$	$ \begin{array}{l} -b\{(1/2)(\pi_{2y}+\pi_{5x}+\pi_{3x}+\pi_{6y})\}\\ -b\{(1/2)(\pi_{1y}+\pi_{4x}+\pi_{2x}+\pi_{5y})\}\\ -b\{(1/2)(\pi_{1x}+\pi_{4y}+\pi_{3x}+\pi_{6y})\} \end{array}$	Partly or completely occupied for the d ² , d ⁴ , and d ⁶ configurations of central ions
t _{2g}	$b d_{xy}$ $b d_{xz}$ $b d_{yz}$	$ + (1 - b^2)^{1/2} \{ (1/2)(\pi_{2y} + \pi_{5x} + \pi_{3x} + \pi_{6y}) \} \\ + (1 - b^2)^{1/2} \{ (1/2)(\pi_{1y} + \pi_{4x} + \pi_{2x} + \pi_{5y}) \} \\ + (1 - b^2)^{1/2} \{ (1/2)(\pi_{1x} + \pi_{4y} + \pi_{3x} + \pi_{6y}) \} $	Occupied "
eg	$\begin{array}{c} a d_{x^2 - y^2} \\ a d_{z^2} \end{array}$	$ \begin{array}{c} -(1-a^2)^{1/2} \big\{ (1/2)(\sigma_2 + \sigma_5 - \sigma_3 - \sigma_6) \big\} \\ -(1-a^2)^{1/2} \big\{ (1/\sqrt{12})(2\sigma_1 + 2\sigma_4 - \sigma_2 - \sigma_5 - \sigma_6 - \sigma_3) \big\} \end{array} $	Occupied "
¹ a and b are	the coefficients of mixing of th	e orbitals of the central atom and ligands.	

Fable 4. Molecular σ and π orbitals of octahedra	complexes taking part in the for	rmation of the leading contribution to σ_{para}
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² The subscripts refer to the location of ligands: 1, on the z axis; 2, on the x axis; 3, on the y axis; 4, on the z axis; 5, on the x axis; and 6, on the v axis

But if the magnetic field is oriented perpendicular to the M-F bond, then the symmetry of the system is perturbed and the perturbed states are given by combinations of the ground and excited states. Such mixed states describe some orbital motion of electrons (or the orbital paramagnetic current). The local magnetic fields generated in the nuclei in this case are determined by the current components related to individual atoms, and these components can have different signs in the general case of heteroatomic compounds. As we show in Section 3.2, the induced magnetic fields in the nuclei can be both codirected with the external magnetic field and directed opposite to it, which can lead to both an enhancement of the magnetic field (paramagnetism) and its weakening ('demagnetization'). Such processes can result in the appearance of shifts of the NMR signals toward both weaker and stronger magnetic fields.

The expression for the transverse (with respect to the M-F bond) and isotropic component of the shielding tensor obtained by Ramsay in the most general case can be represented as [29]

$$\sigma_{\text{orb}\,\perp} = -\left(\frac{he}{mc}\right)^2 \sum_n (E_n - E_0)^{-1} |\langle 0|L|n\rangle ||\langle 0|Lr^{-3}|n\rangle| + \text{c.c.},$$

$$\sigma_{\text{isotr}} = \frac{2}{3} \sigma_{\text{orb}\,\perp},$$
(5)

where E_0 , E_n , $\langle 0 |$, and $|n \rangle$ are the eigenfunctions and eigenvalues of the ground and excited states of the unperturbed system (molecule or crystal), L is the orbital angular momentum relative to the nucleus, and c.c. stands for complex conjugation. The first matrix element in (5) describes the current that arises in the system under the effect of a magnetic field, and the second matrix element describes the magnetic field produced by this current at the location of the nucleus. The above-noted ambiguity in the directions of the shifts of the NMR signals (toward both weaker and stronger magnetic fields) is due to the contribution of the matrix element $|\langle 0|Lr^{-3}|n\rangle|$.

3.2 Effect of antibonding d electrons on the orbital component of the magnetic shielding of the fluorine nuclei in octahedral $[MF_6]^{n-}$ groups

The common character of the energy spectrum and the wave functions of octahedral molecules and complex ions have been well studied. Figure 4 schematically shows the molecular orbitals of an M-F fragment in an octahedral MF_6 grouping and the general layout of the energy levels of this group. In the layout, the Fermi level lies between the levels of binding $\left(t_{2g}\right)$ and antibinding (t_{2g}^*) orbitals.

The detailed expressions of the molecular σ and π orbitals of the octahedral complex that take part in the formation of the leading contributions to the paramagnetic component of shielding σ_{para} are given in Table 4. To calculate the components of the tensor of shielding of nuclei with formula (5), it is suitable to use the rules for the action of the orbital moment operators on the atomic p and d orbitals, which are given in the form of 'multiplication tables' in Table 5.

For complexes of ions of transition metals with unoccupied d shells (the electron configuration d⁰), the upper occupied orbitals are the binding t_{2g} orbitals (see Fig. 4). The chemical shift in this case is due to the mixing of this t_{2g} state (of the π type) with the unoccupied antibinding e_{σ}^* state of the σ^* type, which is schematically shown in Fig. 4a. For the octahedral complexes in this case, the magnitude of ΔE is several tens of thousand cm⁻¹ ($\Delta E = 10Dq$) (see Tables 2 and 3), meaning that at a qualitative level, the shielding



Figure 4. Diagrams of the energy levels and the molecular orbitals of MF_6 molecules with the configurations of the central atoms d^0 (a) and d^6 (b). The vertical solid arrows connect the states that are mixed under the effect of the angular momentum operator. The action of the operator L_z on the orbitals t_{2g} and t_{2g}^* is shown by arched arrows.

	p_x	p_y	p_z	d_{z^2}	d_{yz}	d_{xz}	d _{xy}	$d_{x^2-y^2}$
$egin{array}{c} L_x \ L_y \ L_z \end{array}$	$\begin{array}{c} 0\\ p_z\\ 0 \end{array}$	$-p_z$ 0 p_x	$ \begin{array}{c} p_y \\ -p_x \\ 0 \end{array} $	$ \begin{array}{c} \sqrt{3} \mathrm{d}_{xz} \\ -\sqrt{3} \mathrm{d}_{yz} \\ 0 \end{array} $	$\frac{d_{xy}}{\sqrt{3} d_{z^2} - d_{x^2 - y^2}} \\ - d_{xz}$	$\begin{array}{c} -(\sqrt{3}d_{z^2} + d_{x^2 - y^2}) \\ -d_{xy} \\ d_{yz} \end{array}$	$\begin{array}{c} -\mathrm{d}_{yz} \\ \mathrm{d}_{xz} \\ 2\mathrm{d}_{x^2-y^2} \end{array}$	d_{xz} d_{yz} $-2d_{xy}$



Figure 5. Circulation of electrons corresponding to the $\pi \to \sigma^*$ and $\pi^* \to \sigma^*$ excitations in an F-*M* fragment under the effect of an exciting magnetic field H_0 .

constant for the diamagnetic complexes of ions of transition metals should correspond to an enhancement of the magnetic field at the location of the nucleus, i.e., to paramagnetism, and to a shift of the NMR signals toward weaker fields.

For the $[MF_6]^{n-}$ molecules and complexes containing central ions with the electron configuration d⁶, the occupied state is the antibonding t_{2g}^* state of the π^* type, which lies above the Fermi level (Fig. 4b). Under the action of the angular momentum operator, the e_g^* state mixes with both the t_{2g} state and the t_{2g}^* state. It can be seen that the contribution from this new source of shielding can be substantial, because *a priori* $\Delta E_2(t_{2g}^* \to e_g^*) < \Delta E_1(t_{2g} \to e_g^*)$.

Qualitatively, it can also be seen that these two contributions are subtracted rather than added, which was first noted in [13] within the approach described in the earlier study [47]. The direction of the circulation of electron currents caused by the mixing of t_{2g} and e_g^* states is identical for both the ligands and the central atom (Fig. 5a). In mixing the t_{2g}^* and e_g^* states, these directions must be opposite, as is shown in Fig. 5b.

Because the molecules and the complex ions are weak paramagnets on the whole, the direction of the circulation of the orbital current in the system corresponds to paramagnetism, i.e., to a clockwise circulation. This direction is always controlled by the less electronegative element, which in this case is the central atom. If the central ion is in the occupied antibonding state t_{2g}^* (the electron configuration d⁶), then a 'demagnetizing' orbital current arises at the ligand atoms, with the circulation direction opposite to that in the central atom (Fig. 5b). Consequently, the paramagnetic component of shielding, which is caused by mixing the t_{2g}^* and e_g^* states, can change sign, which leads to a shift of the NMR signals of ¹⁹F (and other anions) toward stronger fields (with respect to the NMR signals of diamagnets).

3.3 Analysis of magnetic shielding of ¹⁹F nuclei in $[MF_6]^n$ groups

based on the density functional theory

Modern methods for quantitatively analyzing the magnetic shielding of nuclei were developed in [48–50]. These methods are based on the density functional theory (DFT) realized in the ADF-2008 program package [31–33]. The interest in the DFT [51–54] rapidly increased because of a substantial increase in the speed and accuracy of quantum calculations as compared to those used in other efficient methods (Hartree–Fock, Møller–Plessett, and so on). Table 6 lists the results of our DFT calculations of the parameters of molecules and nuclear magnetic shielding tensors for ¹⁹F nuclei in isolated $[MF_6]^n$ groups.

A qualitative agreement of the calculated parameters with the experimental data, including those related to the effect of antibonding d^4 and d^6 electrons, can be noted. This fact confirms the model of orbital currents caused by the mixing of the ground and excited states under the effect of a magnetic field.

3.4 Antibonding d^n electrons in octahedral $[MF_6]^{n-1}$ and cuboctahedral Mo_6S_8 groups

in the method of the electron localization function

One of the most demonstrative methods of analyzing electron density, including antibonding electrons, is the electron

Molecule,	Electron		D (1	M-F), Å	$-\sigma_{\parallel}$ (19)	F), ppm	$-\sigma_{\perp}$ (¹⁹	F), ppm			
molecular ion	of central ion	U, ev	Calculation	Experiment [40]	Calculation	Experiment	Calculation	Experiment			
WF ₆	5d ⁰	-40.8	1.859	1.826	333.2	230	615	440			
MoF ₆	4d ⁰	-38.4	1.861	1.815	440	245	753	530			
TeF ₆	4d ¹⁰	-26.4	1.889		115	133	564	350			
PtF ₆	5d ⁴	-23.8	1.895	1.850	4080	6900	1600	3700			
$[IrF_6]^-$	5d ⁴	-33.9	1.925		2280	3360	900	1900			
$\left[OsF_{6}\right]^{2-}$	5d ⁴	-34.8	1.995		1370	1880	430	1240			
$\left[RuF_{6}\right]^{2-}$	$4d^4$	-33.6	1.979		4920	9820	1004	5300			
$\left[\mathrm{NiF}_{6} ight]^{2-}$	3d ⁶	-29.6	1.832		39	210 ± 20	-122	-200 ± 20			
$\left[PdF_{6} ight] ^{2-}$	4d ⁶	-27.3	1.975		6	180 ± 20	-110	-180 ± 20			
$[RhF_6]^{3-}$	4d ⁶	-24.7	2.084		11	100 ± 5	-460	-422 ± 5			
$\left[PtF_{6} ight] ^{2-}$	5d ⁶	-29.9	1.996			160 ± 20		-230 ± 20			

Table 6. Results of our calculations of the parameters of octahedral $[MF_6]^{n-1}$ groups in comparison with experimental data



Figure 6. (See in color online.) Isosurfaces of the electron localization functions (ELFs) of (a) WF_6 and (b) PtF_6 molecules calculated using the same value of ELF (0.65). In the equatorial planes, ELF maps are shown.

localization function (ELF) method that was suggested in [55] based on the Hartree–Fock theory of the self-consistent field and was later modified for the DFT [56]. In this method, the function

$$\mathrm{ELF}(\mathbf{r}) = \left[1 + \left(\frac{D(\mathbf{r})}{D_{\mathrm{h}}(\mathbf{r})}\right)^{2}\right]^{-1} \tag{6}$$

is analyzed, with

$$\begin{split} D(\mathbf{r}) &= \frac{1}{2} \sum_{j=1}^{N} \left| \nabla \varphi_{j}(\mathbf{r}) \right|^{2} - \frac{1}{8} \frac{\left| \nabla \rho(\mathbf{r}) \right|^{2}}{\rho(\mathbf{r})} ,\\ D_{\rm h}(\mathbf{r}) &= \frac{3}{10} \left(3\pi^{2} \right)^{2/3} \rho^{5/3}(\mathbf{r}) , \qquad \rho(\mathbf{r}) = \sum_{j=1}^{N} \left| \varphi_{j}(\mathbf{r}) \right|^{2} , \end{split}$$

where $\rho(\mathbf{r})$ is the electron density, $D_h(\mathbf{r})$ is the kinetic energy density for the homogeneous Thomas–Fermi electron gas, and $D(\mathbf{r})$ is the excess density of the local kinetic energy of electrons (fermions) caused by Pauli repulsion with respect to the density of the local kinetic energy of bosons; the summation ranges over all N molecular orbitals φ_i .

It follows from (6) that the value $\text{ELF}(\mathbf{r}) \approx 0.5$ is realized at those points of space where $D_h(\mathbf{r}) \approx D(\mathbf{r})$ and the electron density is close to the density of a homogeneous electron gas. This means that the isosurface with $\text{ELF}(\mathbf{r}) \approx 0.5$ corresponds to the Fermi surface of the system under consideration. It can also be seen that the regions in which $D(\mathbf{r}) > D_h(\mathbf{r})$ and $\text{ELF}(\mathbf{r}) < 0.5$ correspond to the distribution of delocalized electrons, and the regions where $\text{ELF}(\mathbf{r})$ has values from 0.5 to 1.0 correspond to the distribution of electrons with a high degree of localization of electron pairs with antiparallel spins ('bosons').

Therefore, the $ELF(\mathbf{r})$ function not only efficiently reflects the electron structure and the intramolecular and intermolecular interactions but also is a suitable tool for the analysis of distributions of antibonding electrons and unshared electron pairs in atomic and molecular systems.

For mapping $\text{ELF}(\mathbf{r})$, the use of color isolines was proposed in [56]. The isolines corresponding to the $\text{ELF}(\mathbf{r})$ values in the range from 0.5 to 1.0 are shown using various tints of blue. These isolines characterize the distribution of the degree of localization of unshared electron pairs in anions and of antibonding electrons in cations. The regions of $\text{ELF}(\mathbf{r})$ in the range from 0 to \approx 0.5, which are shown by various tints of red and yellow, refer to the entire spectrum of delocalized electrons of covalent and van der Waals interactions.

Figures 6 and 7 display the ELF maps for the molecules WF₆ and PtF₆; we calculated the ELF isosurfaces in terms of the DFT using the ADF-2008 program package [38, 41–43]. The main feature of the isosurface of the ELF of PtF₆ is a cuboctahedral structure in the vicinity of the central cation Pt⁶⁺, which is absent in WF₆. This structure, which is characterized by ELF(\mathbf{r}) > 0.5, corresponds to the distribution of the degree of localization of antibonding 5d⁴ electrons. It can also be noted that the regions of the maximum localization of the antibonding 5d⁴ electrons are concentrated near the corners of the cube inscribed into the octahedron composed of six F⁻ anions. This feature can be related to the effect of repulsion of the unshared 2p² electron pairs of the [F⁻]₆ ions and the nonbonding 5d⁴ electrons of the central Pt⁶⁺ ions.

An analysis of the ELF also allows revealing the effects of intermolecular interaction. Figure 7b shows an ELF(\mathbf{r}) map calculated for a group of nine PtF₆ molecules located in the corners and at the center of the unit cell of a body-centered cubic (bcc) structure [in the section by the (110) plane]. The character of the ELF(\mathbf{r}) in the region of the intermolecular contacts F \cdots F indicates a van der Waals interaction (yellow isolines) and a weak exchange interaction characterized by common isolines in this region that bound the so-called 'bond path' [56].

Another contribution to the intermolecular interaction of PtF_6 molecules can arise because of a partial overlap of the regions of maximum localization of nonbonding $5d^4$ electrons of the central Pt^{6+} ion that are elongated in the direction of eight Pt^{6+} ions located at the corners of the bcc unit cell. No such overlap has been revealed within the accuracy of the calculations performed, which probably can be explained by the large magnitude of Pt-Pt spacings.

The possibility of the existence of a finite overlap of nonbonding d⁴ electrons follows from the results of calculations of the cuboctahedral molecule Mo_6S_8 (Fig. 8). In these molecules, the Van Vleck Mo^{n+} ions with electron configurations 4d⁴ (4Mo²⁺) and 4d² (2Mo⁴⁺) are located near the centers of the faces of the cube formed by eight S²⁻ ions. The intramolecular spacings D(Mo-Mo) = 2.66 Å are then almost two times greater than the sum of the ionic radii of



Figure 7. (See in color online.) ELF maps in the unit cell of the bcc structure of (a) WF_6 and (b) PtF_6 .



Figure 8. (See in color online.) ELF map of a cuboctahedral Mo_6S_8 molecule in the sagittal section containing four Mo atoms. The S atoms (smaller spheres) are located below and above the 4Mo plane. Symmetry O_h ; D(Mo-S) = 2.467 Å, D(Mo-Mo) = 2.665 Å; energy of formation $U(Mo_6S_8) = -98.41$ eV.

Mo²⁺ and Mo⁴⁺. Nevertheless, the ELF map shown in Fig. 8 demonstrates a strong Mo−Mo exchange interaction, which is characterized by the formation of regions of closed isolines, or the so-called disynaptic reservoirs inherent in covalent bonds [56]. It can also be noted that the intermolecular contacts Mo−Mo in Mo₆S₈ crystals are somewhat greater (by \approx 5%) than the intramolecular spacings D(Mo-Mo) = 2.66 Å, but Mo₆S₈ and Mo₆Se₈ are respectively characterized in this case by metallic and half-metallic properties [17], which are related to the intramolecular and intermolecular overlaps of the 4d_{z²} orbitals Mo−Mo at

distances that substantially exceed the ionic radii of the $Mo^{2+} \mbox{ and } Mo^{4+} \mbox{ cations}.$

Returning to the problem of the possible overlap of the orbitals of the antibonding $5d^4$ electrons of the Pt⁶⁺ ions in the molecular crystal PtF₆, we note that the intermolecular spacings Pt–Pt are approximately two times greater than the Mo–Mo spacings in Mo₆S₈ and approximately four times greater than the sum of the ionic radii of the Mo²⁺ and Mo⁴⁺ ions. Since the wave functions depend on the spacing exponentially, it can be expected that not only upon a twofold but even upon a fourfold increase in the distances between the Van Vleck Pt⁶⁺ ions their exchange interaction is not vanishingly small.

4. Intermolecular interaction in systems with antibonding dⁿ electrons

As was noted above, the ions of transition metals with an even number of electrons in their partly occupied d shells can frequently be characterized by a singlet ground state and a zero magnetic moment. In molecular systems containing such ions, the d electrons occupy antibinding orbitals and are therefore antibonding. The magnetic fields of the nuclear spins perturb the ground state, mix it with the excited states, and 'induce' the appearance of nonzero magnetic moments of ions. It seems unexpected that such a disturbance also results in the appearance of additional contributions to the intermolecular interaction (considered in Sections 4.1–4.3).

4.1 Volatility of molecular hexafluorides

The existence of unusual forces of cohesion between the molecules of platinoid-metal hexafluorides follows from the data on the volatilities of their crystals. The volatilities of molecular substances (and the vapor pressures p over them) are directly determined by the energy of the intermolecular interaction, or more precisely, by the work of evaporation U' of the molecules of their crystals into the gas phase:

$$\ln \frac{p}{p_0} = -\frac{U'}{RT},\tag{7}$$



Figure 9. Vapor pressure *p* over transition-metal hexafluorides and xenon. T = 288 K, $p_0 = 1$ atm. For the hypothetical compound PdF₆, the extrapolated value of p/p_0 [10] is given.

where *R* is the gas constant, *T* is the absolute temperature, and p_0 is the vapor pressure at $T \rightarrow \infty$. Figure 9 displays experimental data on the dependence of the vapor pressure of the hexafluorides of transition and actinide elements (and also xenon) on the degree of population of their d shells (for Xe, of its outer 5s shell) [10].

The anomalously low volatility of solid XeF₆ is explained by the fact that according to the XRD data in [57, 58], its crystal structure does not contain discrete XeF₆ molecules, but is formed by tetrameric $[XeF_6]_4$ molecules, which appear to be stabilized by direct electron-deficit Xe – Xe bonds [39]. It is obvious that the evaporation of monomeric XeF₆ molecules from such a crystal is hampered by the necessity of preliminarily breaking intramolecular bonds in tetramers. This fact is an independent confirmation of the conclusion that certain contributions to the intermolecular interaction related to the electron configurations of the central ions exist in hexafluorides of transition metals.

At the same time, it seems unexpected that the parameters of the volatility in the series of isostructural hexafluorides WF₆, ReF₆, OsF₆, IrF₆, and PtF₆ (see Fig. 9) vary almost monotonically as the number of $4d^n$ and $5d^n$ electrons increases and are independent of whether the ground state of these molecules is spin-paired (PtF_6) or spin-nonpaired (as in the triads Tc, Ru, Rh and Re, Os, Ir). These facts could be interpreted as supporting the model of the higher-spin state of the central Pt⁶⁺ ion with its 5d⁴ configuration, but this contradicts both the NMR data and the magnetic properties of PtF₆, which indicate the temperature-independent (Van Vleck) paramagnetism. According to these data, the ground state of PtF_6 is mixed, and the admixture of the nonpaired spin density transferred from the Pt^{6+} ions to the 2s orbitals of the F^- ions is small (0.58%). A possible explanation of this paradox may lie in the fact that for Curie-Weiss paramagnets, which include TcF₆, RhF₆, ReF₆, and IrF₆, the fraction of spin density transferred from the central ions to the 2s orbitals of the ligands (F^{-}) is also small and its magnitude is proportional to the number of d electrons [39]. But in this case, we should assume that the transfer of spin density to the atoms of ligands is independent of whether the spin state of the central ion is pure (for odd *n*) or mixed (for systems with even *n*).

4.2 Melting and boiling temperatures of molecular hexafluorides

The intermolecular interaction energy U can also be estimated from the data on the melting temperatures of crystals $T_{\rm m}$ based on the Lindemann formula $T_{\rm m} = cUv^{2/3}$ [57], where c is a constant, assumed to be identical for crystals with a similar structure, and v is the molar volume. The melting temperatures of molecular crystals WF₆ and PtF₆ are respectively 275 and 334 K according to [11]. The structures and the molecular volumes of these crystals virtually coincide; consequently, the energy of intermolecular interaction U(PtF₆) is approximately 20% greater than U(WF₆).

Figure 10 presents the dependences of the thermodynamic parameters of isostructural hexafluorides of platinum-group metals on the number of electrons in the 4d and 5d shells of the central ions according to [11]. From the diagram displayed, a paradoxical conclusion follows that the melting temperatures of platinum hexafluoride and palladium hexafluoride are proportional to the index n, the number of electrons at the central ion $(4d^n, 5d^n)$. Special attention should also be paid to the fact that the boiling temperatures of the hexafluorides vary symbatically with the melting temperatures. This means that the intermolecular interaction of the hexafluorides of transition metals is proportional to the number of antibonding 4d and 5d electrons of the central ions, in complete agreement with the data on the volatilities of their crystals. Therefore, the antibonding electrons in hexafluorides of transition metals decrease the energy of the intramolecular interaction but increase the energy of intermolecular interaction.

We also note a feature related to the weak dependence of the temperatures of solid-state $\alpha \leftrightarrow \beta$ transformations on *n*, i.e., on the number of 4d^{*n*} and 5d^{*n*} electrons at the central ions. As can be seen from Fig. 9, the temperatures of the polymorphic $\alpha \leftrightarrow \beta$ transitions for the hexafluorides of platinoid metals are virtually insensitive to the variation of the number of antibonding electrons *n*.

At first glance, this result contradicts the data on the dependence of the energy of the intermolecular interaction on n. But this contradiction can be eliminated if we assume



Figure 10. Dependence of the temperatures of melting $T_{\rm m}$ (\odot), boiling $T_{\rm boil}$ (\bullet), and polymorphic $\alpha \leftrightarrow \beta$ transformations in a series of transitionmetal hexafluorides on the number *n* of (a) 5d^{*n*} and (b) 4d^{*n*} electrons.

that the polymorphic $\alpha \leftrightarrow \beta$ transitions in the hexafluorides of platinoids are related to the intramolecular transformations in *M*F₆ molecules, which are due to the Jahn–Teller effect [59]. As is known [60–62], the high (O_h) symmetry of the octahedral *M*F₆ molecules can be achieved by using hybrid d²sp³ orbitals of the central atom. However, because of the pseudodegeneration effect, this type of hybridization turns out to be unstable with respect to the transition to the hybridization of sd⁵-type orbitals, in which case the location of the six ligands corresponds to a distorted octahedron [60].

4.3 Intramolecular and intermolecular spacings in molecular hexafluorides

According to the data of high-precision XRD studies of a number of hexafluorides of transition metals performed on single crystals in [40], the isostructural crystals PtF_6 and WF_6 belong to the orthorhombic system (space group *Pnma*; four molecules in the unit cell). The lattice parameters at T = -140 °C are as follows:

for PtF_6 ,

$$a = 9.374 \text{ Å}, \quad b = 8.527 \text{ Å}, \quad c = 4.933 \text{ Å},$$

 $V_0 = 394.32 \text{ Å}^3, \quad \langle D(\text{Pt}-\text{F}) \rangle = 1.848 \text{ Å};$
for WF₆,

$$a = 9.466 \text{ Å}, \quad b = 8.608 \text{ Å}, \quad c = 4.988 \text{ Å},$$

 $V_0 = 406.44 \text{ Å}^3, \quad \langle D(W-F) \rangle = 1.823 \text{ Å}.$

From the analysis of interatomic spacings, it has been deduced that the average intramolecular spacings are $\langle D(\text{Pt}-\text{F})\rangle_{\text{exp}} = 1.850 \text{ Å}$ for PtF_6 (the calculated value is 1.895 Å) and $\langle D(\text{W}-\text{F})\rangle_{\text{exp}} = 1.823 \text{ Å}$ for WF_6 (the calculated value is 1.859 Å). The difference between the calculated and experimental values of D(M-F) is explained by the contribution of molecular librations, whereas the change ΔD in this spacing in passing from WF₆ to PtF_6 , which is $\Delta D = 0.027 \text{ Å}$ in experiments (the calculated value is 0.036 Å), can only be due to the effect of repulsion forces generated by the antibonding 5d⁴ electrons of the Pt^{6+} ion.

At the same time, it can be seen from the data given that all three lattice parameters (a, b, and c) of PtF₆ are smaller than those of WF₆ and, correspondingly, the volume per PtF₆ molecule (98.58Å³) is less than that per WF₆ molecule (101.60Å³) by 3.03Å³. As was noted in [39], the directions and the number of intermolecular F...F contacts are identical in both crystals. This means that the observed changes in the parameters can only be due to a decrease in the intermolecular F...F spacings, which agrees with the data of the analysis of the ELF (see Fig. 7).

Therefore, the results of high-precision XRD studies of WF_6 and PtF_6 single crystals [40] give one more experimental confirmation of the existence of intermolecular cohesion forces caused by the effect of antibonding 5d⁴ electrons of Van Vleck Pt⁶⁺ ions.

At the same time, it seems unexpected that the volumes of the unit cells and the average M-F spacings in the series of isostructural hexafluorides change almost monotonically as the number of $5d^n$ and $4d^n$ electrons increases (Figs 11a and 11b) and are independent of whether the ground state of these molecules is spin-paired (for PtF₆) or spin-unpaired (for the triads of Tc, Ru, Rh and Re, Os, Ir hexafluorides). As was noted in Section 4.2, this paradox can be explained by the fact that in Curie–Weiss paramagnets, such as TcF₆,



Figure 11. Dependences of the volumes of the unit cells and intramolecular spacings M-F in $5d^n$ (a) and $4d^n$ (b) hexafluorides on the number of antibonding electrons *n*.

RhF₆, ReF₆, and IrF₆, the fraction of the spin density transferred from the central ions onto the 2s orbitals of the ligands (F^-) is also small and its magnitude is proportional to the number of d electrons [39]. But in this case, we should assume that the transfer of spin density to the ligand atoms is independent of whether the spin state of the central ion is pure (for odd *n*) or mixed (for systems with even *n*). In both cases, the appearance of cohesion forces related to the effect of 5dⁿ and 4dⁿ electrons can be caused by the pairing of the induced spin density of F^- ions of adjacent MF_6 molecules.

5. Chevrel phases and other metal cluster compounds containing octahedral groups of transition-metal ions with partly occupied dⁿ shells

Some molybdenum chalcogenides, such as the binary Mo_6X_8 (X = S, Se, Te) and intercalation MMo_6X_8 (M = Mg, Sn, Pb, etc.) [19] and $M_2Mo_6X_8$ [63–73] compounds, are called Chevrel phases. The interest in Chevrel phases is related to their potential for the development of superconducting solenoids [19, 20], cathode materials [63–73], various nano-devices, molecular 'engines' [74], and so on.

Compounds related to Chevrel phases are formed from cuboctahedral Mo_6X_8 molecules and $[Mo_6X_8]^{n-}$ molecular ions (Fig. 12), including Mo^{2+} and Mo^{4+} ions with the electron configurations $4d^2$ and $4d^4$ with an even number of electrons in partly occupied d shells. The Mo^{2+} and Mo^{4+} ions are located near the centers of the faces of trigonally distorted cubes formed by X^{2-} anions such that two of eight anions lie on the C₃ axes (marked by solid triangles in the figure) and six X^{2-} anions are located in random positions.

The crystal structure of Chevrel phases refers to a slightly (rhombohedrally) distorted CsCl type ($\mathbf{R}\bar{3}$) in which the position with the coordinates (000) is vacant (in binary systems) or is occupied by M atoms (in ternary MMo_6X_8



Figure 12. (a) Packing of Mo_6X_8 molecules around the central vacancy (circle shown by a dashed line) in binary Chevrel phases. (b) Unit cell of ternary MMo_6X_8 compounds. Dotted lines correspond to the intermolecular Mo-X bonds and thin lines, to the intermolecular Mo-Mo bonds; D(Mo-Mo) = 2.836 Å, $D_{in}(Mo-Mo) = 2.684$ Å (in Mo_6Se_8).

systems); the rhombohedral angle is $\approx 89.5^{\circ}$. Mo₆ X_8 cuboctahedra are connected by Mo–Mo intermolecular bonds, whose length D(Mo-Mo) = 2.836 Å exceeds the length of the intramolecular bonds $D_{in}(Mo-Mo) = 2.684$ Å (in Mo₆Se₈) by only $\approx 5\%$. In addition, all Mo atoms form short intermolecular bonds with the X atoms that lie in random positions, thereby forming a rigid three-dimensional framework. It turns out that the structure of binary Chevrel phases is in fact pseudomolecular and no effects of orientational disorder [25], inherent in systems with highsymmetry octahedral MF_6 molecules in solids [75], are revealed in them.

Another type of ordering is related to formally fractionalvalence states of ions [76] represented by $[Mo]^{x+}$ ions in both binary and ternary systems. However, the structural and magnetic properties of Chevrel phases [17, 22] evidence in favor of electron structures with an even number of electrons in partly occupied d shells and the related charge disordering of Mo⁴⁺ and Mo²⁺ ions. The ratio of these ions should be 2 : 4 in binary compounds and 1 : 5 in ternary compounds. Only for the compound SnMo₆X₈, for which the charge state of tin can be Sn⁴⁺, is a charge-homogeneous distribution of Mo²⁺ ions possible. The variability of the oxidation state related to the transitions between 4d² \leftrightarrow 4d⁴ electron configurations (characteristic of Van Vleck ions of transition metals) are one of the essential elements that determine the intermolecular interaction and properties of compounds of this type.

5.1 Magnetic shielding of ⁹⁵Mo nuclei in Chevrel phases

The nearest neighborhood (coordination shell) of $[Mo]^{n+}$ ions in the Chevrel phases consists of five X^{2-} anions located in the corners of a slightly distorted square pyramid of idealized symmetry C_{4v} (see Fig. 12). Four of these X^{2-} anions in the base of the pyramid belong to a cuboctahedral molecule or an $[Mo_6X_8]^{x-}$ molecular ion (x = 0, 2, 4) and the apex of the pyramid is occupied by an X^{2-} anion of the neighboring $[Mo_6X_8]^x$ group. The crystal field of the square-pyramidal surroundings splits the d level of the central $[Mo]^{n+}$ ion into four sublevels, of which the main level is a $\mathrm{U}_{3/2g}$ doublet constructed from the d_{xz} and d_{yz} orbitals. The excited level nearest to the main level is an $E_{5/2g}$ singlet (d_{xy}) separated from the ground state by the large gap $\Delta E = 3.71 Dq$. For the electron configuration d^4 of the central ion, the level $U_{3/2g}$ is the highest occupied and nongenerate state, and the $E_{5/2g}$ level is the lowest unoccupied state. Under the effect of a magnetic field, these states can mix, but the expected values of the induced magnetic fields in the ⁹⁵Mo nuclei are small, which is caused by the large value of ΔE . This conclusion appears to qualitatively agree with the experimental NMR data for ⁹⁵Mo in SnMo₆S₈ (Table 7), for which an Sn⁴⁺ charge state of tin and, consequently, a homogeneous charge distribution of Mo²⁺ ions with electron configurations 4d⁴ can be supposed to exist.

For the binary compounds Mo₆Se₈ and Mo₆Te₈ containing Mo^{4+} ions with electron configurations $4d^2$, the induced magnetic field at the ^{95}Mo nuclei can be comparable with the value found for ^{51}V nuclei of the impurity V^{3+} ions (the electron configuration $3d^2$) in the structure of corundum Al₂O₃ [2] (see Table 1). In the case of a charge-ordered distribution of the Mo²⁺ and Mo⁴⁺ ions, the NMR spectrum of ⁹⁵Mo should be represented by two lines with the intensity ratio 2:1, of which the most intense line (of Mo^{2+} ions), as in the case of $SnMo_6S_8$, is characterized by a small absolute value of σ . For a dynamically disordered distribution, the averaged spectrum consists of a single line in the center of gravity of the initial spectrum with the magnitude of the magnetic shielding constant $\langle \sigma \rangle \approx 1/3 \sigma (Mo^{4+})$. Because only single NMR lines of ⁹⁵Mo in Mo₆Se₈ and Mo₆Te₈ were found in the experiments in [26], this result can be considered an indication of the existence of a dynamically disordered charge distribution caused by the fast electron exchange $Mo^{2+} \leftrightarrow Mo^{4+}$.

We also note that the experiments in [26] revealed an axial symmetry of the magnetic shielding tensor of the 95 Mo nuclei in binary compounds Mo₆Se₈ and Mo₆Te₈ (see Table 7). This result seems to be unexpected, since the second coordination shell of Mo ions, which includes 4 Mo (see Fig. 12), is essentially nonaxial. This fact can indicate a small magnitude of the contribution to the magnetic shielding related to the intermolecular Mo–Mo interaction. This interaction, which perturbs the axial symmetry of the second coordination shell, is related to the electric conductivity of the Chevrel phases, including the binary compound Mo₆S₈. However, Mo₆Se₈ is a half-metal, whereas Mo₆Te₈ is a semiconductor; therefore, it is possible that the contribution to magnetic shielding associated with the intermolecular Mo–Mo interaction is not substantial.

Table 7. Components of the magnetic shielding tensors of ⁹⁵Mo nuclei in compounds of the Chevrel-phase group.

Compound	Mo ₆ Se ₈ [26]	Mo ₆ Te ₈ [26]	Pb _{1.125} Mo ₆ S _{7.5} [23]	SnMo ₆ S ₈ [21]	Sn _{1.2} Mo _{6.5} Se ₈ [23]
Electron configuration of [Mo] ^{x+}	$(4d^2)_2 + (4d^4)_4$	$(4d^2)_2 + (4d^4)_4$	$(4d^2)_1 + (4d^4)_5$	$4d^4$	$4d^4$
$-\sigma_{\parallel}, \mathrm{ppm}$	545	3050	—	330	—
$-\sigma_{\perp}, \mathrm{ppm}$	2200	4900		730	
$-\sigma_{\rm isotr}$, ppm	1650	4280	3500	600	2100



Figure 13. (a) Temperature dependence of the magnetic shielding constants of ⁷⁷Se nuclei in Mo_6Se_8 and $SnMo_6Se_8$ according to [22]. (b) ¹²⁵Te NMR spectra in binary compounds Re_6Te_{15} [13] and Mo_6Te_8 [12] and in the $Cs_4[Re_6Te_8(CN)_6]$ complex [13].

5.2 Magnetic shielding of ¹²⁵Te nuclei in Chevrel phases and in other metal cluster compounds

containing octahedral groups of transition-metal ions

More information on the character of the electron structure of cuboctahedral metal clusters can be extracted from the data on the magnetic shielding of the ³³S, ⁷⁷Se, and ¹²⁵Te nuclei of the diamagnetic ligands in the composition of the Chevrel phases and other metal cluster compounds, including octahedral (predominantly, mixed-valence) groups of transition-metal ions with electron configurations d² and d⁴ [12–16, 21–25, 27].

For ternary Chevrel phases, there are characteristic small values of the magnetic field enhancement coefficients at the points of location of the nuclei of nonmagnetic ligands Se²⁻ $(\sigma_{isotr} = -200 \text{ ppm in Pb}_{1.125}\text{Mo}_6\text{Se}_{7.5} \text{ and } \sigma_{isotr} = -500 \text{ ppm}$ in Sn1.2Mo6.5Se8 [23]); for PbMo6S8, magnetic field weakening was also noted in the nuclei of S²⁻ anions $(\sigma_{isotr})^{33}$ S] = +2000 ppm or 0.2% [21]). Such behavior of the magnetic shielding constants can be related to the effects of the occupied antibonding π^* state of cuboctahedral complexes with d⁴ electron configurations in the transition-metal ions. In the atoms of electronegative ligands, a 'demagnetizing' orbital current then arises, whose circulation direction is opposite to that in the ions of electropositive atoms, as is shown in Fig. 5. This means that the paramagnetic component of shielding, which is caused by the mixing of π^* and σ^* states, just as in the case of octahedral complexes, can change sign, leading to a shift of the NMR signals of ³³S, ⁷⁷Se, and ¹²⁵Te (and some other anions) toward higher fields than the NMR signals of diamagnets.

For binary Chevrel phases and other octahedral metal clusters containing ions of transition metals with d^2 electron configurations, more complex effects are observed. The most characteristic features of the shape of the NMR spectra and magnetic shielding of nuclei of diamagnetic ligands in such systems can be demonstrated with the example of the NMR spectra of ¹²⁵Te involved in the nonconducting compounds Mo₆Te₈, Re₆Te₁₅, and Cs₄[Re₆Te₈(CN)₆], shown in Fig. 13. These features could in most cases be caused by the effects of

intermolecular interaction and of charge disordering of the anion positions at high temperatures, and at lower temperatures, by the effects of charge ordering and changes in symmetry [68], whose manifestation can determine the temperature-related changes in the NMR spectra of ⁷⁷Se in Mo_6Se_8 (see Fig. 13).

The nearest neighborhood of the Re^{4+} cations in $\text{Cs}_4[\text{Re}_6\text{Te}_8(\text{CN})_6]$ includes four Te^{2-} anions located on one of the six cube faces (Te₈), and a molecular [CN]⁻ ligand (Fig. 14) located on the fourfold axis that completes the square-pyramidal coordination of Re^{4+} . It follows from a comparison of the maps of the ELF of Mo_6S_8 (see Fig. 8) and [$\text{Re}_6\text{Te}_8(\text{CN})_6$]⁴⁻ (see Fig. 14) that the same type of electron structure with the Re–Re exchange interaction and the formation of 'disynaptic reservoirs' of covalent bonds [56] is observed in these complexes.

The Re³⁺ ions in the Cs₄[Re₆Te₈(CN)₆] complex have the 5d⁴ electron configuration. In this case, as was noted in Section 5.1, the expected values of the induced magnetic dipole moments $\mu_{ion} = \chi_{VV} H$ of the Re³⁺ ions are small,



Figure 14. (See in color online.) ELF maps of the $[(\text{Re}_6\text{Te}_8)(\text{CN})_6]^{4-}$ anion in projections onto the planes (a) (100) and (b) (110). The Re atoms located at the centers of the faces of the cube formed by Te atoms along with the CN anions form octahedra V(Re, Re) inscribed one into another and thus forming a disynaptic reservoir.

which is due to the large value of the excitation energy $\Delta E = 3.71 \, Dq$. But as in the case of the octahedral $[PtF_6]^2$ complexes with the electron configuration 5d⁶ of the central ion (see Fig. 1), the transverse component of the magnetic shielding tensor $\sigma_{\perp}(^{125}\text{Te}) \approx -2700 \text{ ppm}$ is shifted toward stronger magnetic fields compared with the longitudinal component $\sigma_{\parallel}(^{125}\text{Te}) \approx -3000$ ppm. This means that the external magnetic field, just as in the case of $[PtF_6]^{2-}$, induces an orbital 'demagnetizing' current in the atoms of the Te^{2-} ligands whose circulation direction is opposite to that at the central Re atom, as is shown schematically in Fig. 5. On the other hand, for the binary compound Re₆Te₁₅, a shift of the entire ¹²⁵Te NMR spectrum is observed toward weaker magnetic fields relative to the $[Re_6Te_8(CN)_6]^{4-}$ spectrum. Such a shift can be ascribed to an increase in the Van Vleck magnetic susceptibility under the transition of the Re³⁺ cations in $[\text{Re}_6\text{Te}_8(\text{CN})_6]^{4-}$ into the Re^{5+} oxidation state with the electron configuration 5d² in Re₆Te₁₅. Such changes are completely analogous to those in the shielding tensors in molecular hexafluorides (see Table 2 and Fig. 1), caused by the transfer of the induced spin density of Van Vleck ions to the 4s orbitals of the diamagnetic Te^{2+} ligands.

A specific feature of the magnetic shielding of ¹⁹F nuclei in $[PtF_6]^{2-}$ and of ¹²⁵Te nuclei in the $[Re_6Te_8(CN)_6]^{4-}$ complex is the existence of a weakly pronounced fine structure of the ¹²⁵Te NMR spectrum (see Fig. 13) related to a weak (about (0.5°) trigonal distortion of the cuboctahedra. As a result, a physical nonequivalence of the Te²⁻ anions located at the C₃ axes and in random positions (see Fig. 12) arises, with the ratio of the populations equal to 2:6. In the Chevrel phases, the cuboctahedral Mo_6Te_8 molecules are characterized by an analogous $(\sim 0.5^\circ)$ trigonal distortion. But the ^{125}Te NMR spectrum (see Fig. 13) in this case indicates an unexpectedly strong difference between the lines related to the two structural positions of the Te²⁻ anions. The change in the signals from ¹²⁵Te nuclei located on the C₃ axes is relatively small, whereas for the ¹²⁵Te nuclei located in random positions, the isotropic component of the shielding tensor exhibits a jump from the initial value $\sigma_{isotr} \approx -2700$ ppm to $\sigma_{\rm isotr} \approx -4000$ ppm, and the shielding anisotropy $\Delta \sigma$ increases from ≈ 600 to ≈ 2100 ppm. Such a change in the shielding tensor indicates a sharp change in the orbital currents induced in the Te²⁻ ions in random positions, which can be caused by the effect of $(Mo_6Te_8) \cdots (Mo_6Te_8)$ intermolecular interactions (shown in Fig. 12 by dotted lines), which do not affect the Te^{2+} ions on the C₃ symmetry axes.

We note the similarity of the ¹²⁵Te NMR spectra in binary Mo_6Te_8 and Re_6Te_{15} compounds (see Fig. 13), which reflects the similarity of the nearest surroundings of the Re and Mo cations in these two compounds. In both cases, this is a slightly distorted square pyramid with an idealized C_{4v} symmetry formed by anions of two types, apical and facial. The facial anions are located over the faces of the Re₆ and Mo₆ octahedra, and the apical anions are over their apices.

A specific feature of the structure of binary Mo_6X_8 compounds, as can be seen from Fig. 12, is the duality of the disposition of six (of every eight) anions, which are simultaneously both facial (for individual Mo_6X_8 molecules) and apical (in the structure of the crystal as a whole). In Re_6Te_{15} , the apical Te^{2-} anions, in contrast to those in Mo_6Te_8 , do not enter the composition of neighboring cuboctahedral groupings, but occupy the position of the CN^- ligand in the $[Re_6Te_8(CN)_6]^{4-}$ complex. Despite such a difference, the isotropic component σ_{isotr} of the shielding tensor of 125 Te nuclei of the apical ligands in Re₆Te₁₅ (on the C₄ axes) and in Mo₆Te₈ is almost two times greater than the shielding constant of the 125 Te nuclei of the facial ligands (on the C₃ axes). This means that to transfer the spin density of Van Vleck Re and Mo ions onto the diamagnetic Te²⁺ ions, σ -type overlaps are required between the d orbitals of the cations and 4s orbitals of the anions.

At the same time, as was shown in Section 5.1, the antibonding d electrons of the Re and Mo ions populate the atomic d_{xz} and d_{yz} orbitals, which form π^* -type molecular orbitals with the apical and facial ligands Te²⁺. Such orbitals make a contribution to the anisotropic component of the shielding tensor and to the total broadening of the ¹²⁵Te NMR spectrum and do not affect the magnitude of the isotropic component of the shielding tensor. As we show in Section 5.3, the probable mechanism of the appearance of induced magnetic moments in Te²⁺ ions in metal cluster compounds is related to the mixing of d_{z^2} , d_{xz} , and d_{yz} orbitals of the Re and Mo ions under the action of the angular momentum operator.

5.3 Transfer of spin density

and the electric conductivity in Chevrel phases

It follows from the data in Sections 5.1 and 5.2 that the decisive role in the appearance of a substantial difference in the magnetic shielding of Te²⁺ nuclei located in apical (on the C₄ axes) and facial (on the C₃ axes) positions in Re₆Te₁₅ (and in random positions in Mo₆Te₈) is played by the difference in the symmetry of the local positions of the Te²⁻ ions. For the apical positions of the Te²⁺ ligands, an important point is the σ overlap of 4s and 4p_z orbitals with d_{z²} orbitals of Re^{*n*+} and Mo^{*n*+} ions and the formation of σ -type molecular orbitals, analogous to the e_g orbitals in octahedral complexes (see Fig. 4 and Table 4). The magnetic field **H** perturbs these orbitals in accordance with the rules for the action of the angular momentum operator in Table 5:

$$L_x |\mathbf{d}_{z^2}\rangle \rightarrow |\mathbf{d}_{xz}\rangle, \quad L_y |\mathbf{d}_{z^2}\rangle \rightarrow -|\mathbf{d}_{yz}\rangle.$$

As a result of this perturbation, the ground state is mixed with π^* -type excited states (see Table 4) represented by combinations of d_{xz} and d_{yz} orbitals of Re^{n+} and Mo^{n+} with the 4p orbitals of Te²⁻. As a result, the Reⁿ⁺ and Moⁿ⁺ ions acquire 'induced' magnetic moments $\mu_{\text{ion}} = \chi_{VV}H$, and an induced spin density appears on the 4s shells of Te²⁻ ions, which leads to large values of isotropic components of the magnetic shielding tensor σ_{isotr} .

Of special interest is the fact that the magnetic polarization in Chevrel phases and analogous metal clusters can appear only in the presence of mixing of orbitals, including the d_{z^2} orbital of the ground state and d_{xz} and d_{yz} orbitals that are occupied by antibonding electrons of Van Vleck ions. It was noted previously that the d_{z^2} orbitals take part in the formation of spin-paired states of the intercluster Mo–Mo bonds [26], which agrees with the data of DFT calculations and with the results of the analysis of the ELF (see Figs 8 and 14). But the d_{z^2} orbitals of neighboring Mo₆X₈ cuboctahedra do not overlap and the intermolecular Mo–Mo 'bonds' (shown by thin lines in Fig. 12) can be realized only due to the σ overlaps $d_{xz} - d_{xz}$ and $d_{yz} - d_{yz}$.

Therefore, the mixing of d_{z^2} , d_{xz} , and d_{yz} orbitals under the action of the angular momentum operator is important for the electric conductivity of Chevrel phases, which also depends on the intermolecular Mo-Mo spacing and on the degree of overlap of d orbitals.

5.4 Intermolecular interaction in Chevrel phases within the 'atoms-in-molecules' (AIM) method

To analyze the intermolecular interaction in Chevrel phases, we calculated the optimum structure and ELF(**r**) maps of a number of model systems listed in Table 8. Figure 15 displays the structure of the $(Mo_6S_8)_2$ dimer, which was calculated in terms of the DFT [31] using the ADF-2008 program package [32]. The character of the mutual arrangement of atoms and the calculated optimum parameters of the structure of dimers (except for the hypothetical $[(Mo_6S_8)_2]^{8-1}$ anion) are close to those of the $(Mo_6Te_8)_2$ structure.

In the central part of Fig. 15, we show a region of contact of cuboctahedra (monomers) in which intermolecular $Mo \cdots S$ bonds are formed, leading to a 'chemical' nonequivalence of the ions of two structural types of anions, namely, bridge-type, which simultaneously occupy apical and facial positions, and end-type, which occupy only facial positions. Table 8 lists the calculated values of interatomic Mo-X spacings and valence Mo-X-Mo angles in the region of contact of cuboctahedra for the optimized structures of $[(Mo_6X_8)_2]^{n-}$ dimers. We note that the intramolecular and intermolecular Mo-X spacings differ slightly and that the valence angle is substantially less than the optimum value equal to 90° (e.g., the Mo-S-Mo angle is 80.5°).

To analyze the ELF quantitatively, we used Bader's quantum mechanical AIM method [77], which is based on the fundamental principle of stationary action proposed by Schwinger [78]. We used the AIM method [69] based on a topological analysis of the electron density distribution function $\rho(\mathbf{r}, \mathbf{R})$ (\mathbf{r} and \mathbf{R} are the coordinates of electrons and nuclei); the structure and the interatomic interactions are completely determined by the set and types of critical points at which the electron density gradient $\nabla \rho(\mathbf{r}, \mathbf{R})$ vanishes. The second derivatives $\nabla^2 \rho(\mathbf{r}, \mathbf{R})$ (Laplacian) calculated at the critical points form a real symmetric 3 × 3 matrix.

It was established in [77] that in the case of nondegenerate states of the matrix, only four types of critical points of the electron density $\rho(\mathbf{r}, \mathbf{R})$ are possible: (1) points of local maxima, corresponding to the positions of nuclei; (2) change saddle points, characterizing pairwise interactions between atoms; (3) saddle points of the second type, which characterize ring bonds (so-called ring critical points, RCPs); and (4) cell critical points, at which the electron density drops to a local minimum.

Based on the results of DFT calculations of the electron structures of $[(Mo_6X_8)_2]^{n-}$ dimers (X = S, Te), a topological analysis of the $\rho(\mathbf{r}, \mathbf{R})$ function has been performed using the



Figure 15. Dimer $(Mo_6S_8)_2$ and the location of the ring critical point (RCP) [69]. The dotted lines correspond to the axes of an enhanced electron density $\rho(r)$.

XAIM program (X atoms in molecules) [79]. It was found that the region of contact of Mo_6X_8 cuboctahedra is characterized by a saddle point of the second type (RCP) coinciding with the intersection point of the lines of intermolecular contacts Mo–Mo and X-X (see Fig. 15). The results of calculations and the parameters of the point found are given in Table 8.

The existence of RCPs in the region of contact of cuboctahedra indicates an essentially multicenter (fourcenter) character of the intermolecular interaction of monomers arising in a rhombus-shaped group of four atoms Mo-X-Mo-X. The main parameters of this interaction are the sign and density of the energy of this four-center interaction. The negative sign of the interaction corresponds to attraction; in this case, the main role seems to belong to the relative number of cation positions with the electron configurations d² of Van Vleck ions. The effect of attraction between Mo ions in the boundary group of four atoms Mo-S-Mo-S can explain the decrease in the valence angle Mo-S-Mo to 80.5° compared to the optimum value of 90°.

The results of the calculations agree with the data of the analysis of the magnetic shielding of nuclei, according to which the intermolecular Mo-Mo interaction is related to the mixing of d_{z^2} orbitals with d_{xz} and d_{yz} orbitals, and to the magnitude of induced magnetic moments of Van Vleck ions. It is significant that for the model dimers with charge states 4– and 8–, both the induced magnetic moments and the density of the energy at the RCP are small.

Another parameter that exerts a significant effect on the sign and energy density of the four-center interaction Mo-X-Mo-X seems to be the anion radius, which affects the Mo-Mo distance. In particular, the enhanced ion radius of Te²⁻ (compared to the radius of the S²⁻ anion) can be one of the factors responsible for the repulsive character of the

Table 8. Dependence of the structural parameters of intermolecular contacts and characteristics of ring critical points (RCPs) on the electron configuration of Van Vleck ions in dimers of 6-nuclear clusters $[(Mo_6X_8)_2]^{n-}$ (X = S, Te; n = 0, 4, 8). ρ is the electron density, $\nabla^2 \rho$ is the Laplacian, and *E* is the total energy density.

Dimer	d^2 : d^4	\angle (Mo-X-Mo), deg	D(Mo-X), A	$D(\operatorname{Mo}\cdots X), \operatorname{\AA}$	ρ , a.u.	$\nabla^2 \rho$	E, eV Å ⁻³
$\left(Mo_6S_8\right)_2$	2:4	80.5	2.529	2.559	0.025	0.0353	-0.55
$\left[\left(Mo_{6}S_{8}\right) _{2}\right] ^{4-}$	1:5	85.5	2.586	2.614	0.019	0.0322	-0.11
$\left[\left(Mo_{6}S_{8}\right)_{2}\right]^{8-}{}^{*}$	0:6	—			0.019	0.0335	-0.08
$\left[\left(Mo_{6}Te_{8}\right)_{2}\right]$	2:4	77.9	2.847	2.880	0.019	0.0262	~ 0
$[(Mo_6Te_8)_2]^{4-}$	1:5	80.0	2.896	2.958	0.016	0.0241	0.13
* Without optimization	on; the geo	metric parameters of the	optimized $[(Mo_6S_8)_2]$	^{4–} complex have bee	n postulated.		

energy at the RCP and the absence of metallic conductivity of Mo_6Te_8 . Because a small value of the energy density at the RCP has also been obtained for the dimer $[(Mo_6S_8)_2]^{8-}$, it can be assumed that the change in the charge state of cuboctahedral anion complexes is also significant for the electric conductivity of the ternary Chevrel phases.

6. Single-molecule switch ('nanotransistor') based on a 12-nucleus metal cluster with a variable oxidation state

The results of the analysis of cuboctahedral molecules in the composition of Chevrel phases can serve as a basis for the expansion of the circle of promising single-molecular carriers of electrons and current switches. As an example, we consider the model of a single-molecule transistor based on single π -conjugated organic molecules [80, 81], whose structure reproduces some natural compounds-carriers of electrons in biological systems. Another type of electron carriers is represented by metal cluster compounds, in particular, ferredoxines [82, 83]. The six-nucleus Mo₆ and Re₆ cluster complexes considered in Section 5, whose properties depend on their oxidation state and on the electron configuration of transition-metal ions, can serve as the simplest models of such systems. In particular, 12-nucleus $[Re_{12}CS_{17}(CN)_6]^{n-}$ clusters with a variable oxidation state (n = 6, 8) were considered in [14]. In the unique structure of such clusters, two sixnucleus $[Re_6]$ subunits are connected between themselves through a triangular $[CS_3]^{10-}$ bridge group. The C^{4-} ion in this structure occupies the facial position shared by two $[Re_6]$ subunits, and the S^{2-} ions are in the apical positions shared by two [Re₆] subunits (Fig. 16).

A detailed investigation of structural changes in $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ clusters upon the transition from the degree of oxidation n = 6 to n = 8 was performed [14] by XRD using single crystals of $\text{K}_6\text{Re}_{12}\text{CS}_{17}(\text{CN})_6 \times 20\text{H}_2\text{O}$ and $\text{K}_6\text{Re}_{12}\text{CS}_{17}(\text{CN})_6$. It was shown that a change in the structure of the cluster (see Fig. 16) with the variation in the oxidation degree mainly affects the region of contact of the



Figure 16. Re₁₂CS₁₇ molecule and the location of three RCPs [67]. In the $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$ anion, the cyano groups occupy apical positions near Re^{out} atoms. The dotted lines stand for the axes of an enhanced electron density $\rho(\mathbf{r})$.

triangular $[CS_3]^{10-}$ bridge group with the Re₆ subunits. In the state with n = 6, the Reⁱⁿ \cdots Reⁱⁿ spacing is ≈ 0.3 Å shorter, while the C^{br} \cdots S^{br} spacing is ≈ 0.12 Å longer than that for the cluster with the oxidation degree n = 8 (Table 9). Therefore, with the removal of one pair of d electrons from this cluster, the distance between the nearest Reⁱⁿ atoms of two Re₆ subunits becomes shorter by approximately 10%, which can indicate the appearance of strong attraction, associated with the Reⁱⁿ \cdots Reⁱⁿ electron exchange.

To refine the nature of this attraction, DFT calculations of these structures and of ELF maps have been performed, and they were also analyzed [14-16] using the quantum mechanical AIM method [77]. Of special interest were three rhombus-shaped regions of location of two Reⁱⁿ cations and C^{br} and S^{br} bridge atoms (see Fig. 16) analogous to the location of Mo^{n-} cations and S^{2-} anions in the region of contact of cuboctahedra in the $(Mo_6S_8)_2$ dimer (see Fig. 15). It was found that RCPs, whose parameters are given in Table 9, are located at the centers of the rhombi formed by Reⁱⁿ-C^{br}-S^{br}-Reⁱⁿ The presence of a critical point of this type indicates an essentially multicenter ('threefold four-center') character of the intermolecular interaction of Re₆ monomers in the 12-nucleus Re₁₂CS₁₇ cluster. Judging from the numerical values of the critical point parameters, upon the removal of one pair of d electrons from the $[Re_{12}CS_{17}(CN)_6]^{8-}$ cluster, the energy of the multicenter interaction (attraction) of atoms in the vicinity of this point increases by a factor of 3–4, which can explain the $\approx 10\%$ decrease in the $\operatorname{Re}^{\operatorname{in}} \cdots \operatorname{Re}^{\operatorname{in}}$ distance in $[\operatorname{Re}_{12}\operatorname{CS}_{17}(\operatorname{CN})_6]^6$ (as well as in the $Re_{12}CS_{17}$ molecules).

The change in the degree of oxidation of 12-nucleus clusters between n = 6 and n = 8 is associated with a change in the charge state of one of 12 rhenium ions ($\text{Re}^{3+} \leftrightarrow \text{Re}^{5+}$) and in their electron configuration ($5d^4 \leftrightarrow 5d^2$). As was shown in Section 5.3, such changes in the case of Chevrel phases are accompanied by sharp changes in the magnetic shielding of the nuclei of Van Vleck ions and their ligands. It can be expected that analogous changes also accompany variations in the oxidation degree of 12-nucleus clusters under the transition from n = 6 to n = 8 [76].

To refine the magnetic behavior of 12-nucleus clusters upon the transitions $n = 6 \leftrightarrow n = 8$, $K_6 Re_{12}CS_{17}(CN)_6 \times 20H_2O$ and $K_8 Re_{12}CS_{17}(CN)_6$ polycrystals were studied by the NMR method using ¹³C [14, 16, 84]. The ¹³C NMR spectra of samples enriched with the ¹³C isotope were taken at room temperature using an Avance-400 Bio-Spin (Bruker) spectrometer and a magic-angle spinning (MAS) of the sample at the rotation rate 20 kHz. The spectra obtained are shown in Fig. 17. The shielding constants were determined using an external standard (tetramethyl silane (Si(CH₃)₄), $\sigma_{\text{stand}} = 177.4$ ppm).

The ¹³C NMR spectra of both clusters contain two spectral lines of carbon atoms with the ratio of intensities $\approx 6:1$. In accordance with the formula of these compounds, the more intense line unambiguously refers to carbon atoms

Table 9. Dependence of the intramolecular distances and the RCP parameters on the electron configuration of Van Vleck ions in 12-nucleus metal clusters.

Cluster	d^2 : d^4	$Re^{in}\cdots Re^{in}$	$C^{br}\cdots S^{br}$	σ (¹³ C), ppm	ρ , a.u.	$\nabla^2 \rho$, a.u.	E, eV Å ⁻³
$Re_{12}CS_{17}$	1:11	2.885 Å	3.428 Å	_	0.052	0.102	-2.145
$\left[Re_{12}CS_{17}(CN)_{6}\right]^{6-}$	1:11	2.901 Å	3.454 Å	-257.6	0.046	0.094	-1.65
$[Re_{12}CS_{17}(CN)_6]^{8-}$	0:12	3.168 Å	3.330 Å	157.4	0.034	0.099	-0.55



Figure 17. ¹³C NMR MAS spectra of cluster compounds (a) $K_6Re_{12}CS_{17}(CN)_6 \times 20H_2O$ and (b) $K_8Re_{12}CS_{17}(CN)_6$. The satellite signals caused by the sample rotation are marked by an asterisk (*).

entering the CN^- groups, whereas the less intense line refers to bridging carbon atoms C^{br} .

It is significant that under a change in the charge state of a 12-nucleus cluster, the magnetic shielding of the nuclei of carbon atoms of the apical CN⁻ groups connected with the Re^{out} atoms are virtually unaffected, whereas under the same change in the charge state of the 12-nucleus cluster, a giant jump in the magnetic shielding constant of the nuclei of bridging carbon atoms C^{br} is observed (420 ppm, or 0.042%). Such a jump corresponds to a sharp increase in the paramagnetic component of the susceptibility and the shielding constant of ¹³C^{br} nuclei, and this increase, just as in the Chevrel phases, is related to the transition of one of the six Reⁱⁿ ions nearest to C^{br} from the state with the electron configuration 5d⁴ into the state of a Van Vleck ion with the electron configuration $5d^2$. In other words, the change in the charge state of the cluster is related to the removal of d electrons only from Reⁱⁿ atoms that coordinate the C^{br} atom, whereas the charge state of all six Re^{out} atoms remains unaltered and is equal to +3, which corresponds to the electron configuration 5d⁴ of rhenium atoms.

Of special interest is the problem of sign reversal of the magnetic shielding constant of the nuclei of bridging carbon atoms ${}^{13}C$ for $K_8Re_{12}CS_{17}(CN)_6$. Such behavior of the magnetic shielding constant of the ${}^{13}C$ ^{br} nuclei can be related to the effect of the occupied antibonding π^* state of two cuboctahedral Re₆ subunits that have the electron configurations d⁴ of the constituent cations. In this case, at the more electronegative (compared to Re^{3+} cations) C^{4-} bridging anion under the effect of a magnetic field, an orbital 'demagnetizing' current should be excited whose circulation direction is opposite to the direction of current circulation in Re^{3+} ions, in accordance with the diagram in Fig. 4. This means that the paramagnetic component of shielding caused by the mixing of π^* and σ^* states, just as in the case of octahedral complexes, can change sign and lead to a shift of the NMR signals of ¹³C, as well as of ³³S, ⁷⁷Se, ¹²⁵Te (and other anions) toward stronger fields relative to the NMR signals of diamagnets.

But the most important result of this investigation is the detection (for carbon nuclei) of a giant jump in the magnetic shielding constant of 13 C nuclei in $K_6Re_{12}CS_{17}(CN)_6 \times 20H_2O$. It was noted above that this jump is caused by the transition of one of the six Re^{in} ions nearest to C^{br} from the state with the electron configuration $5d^4$ into a state of a Van Vleck ion with the electron configuration $5d^2$. Because the structure of a given cluster has a symmetry plane in which the atoms of the triangular group of $[CS_3]^{10-}$ bridging atoms are located, we must assume the existence of charge disordering in the $[Re_6^{in}]$ group caused by the electron exchange between two Re_6 subunits. Just as in the case of Chevrel phases, such an exchange can also be realized as a result of mixing of $5d_{z^2}$, $5d_{xz}$, and $5d_{yz}$ orbitals under the effect of the orbital angular momentum operator.

7. Conclusions

The appearance of Van Vleck paramagnetism in all molecular compounds of transition metals containing an even number of electrons in partly occupied d shells can be explained by the mixing of states under the effect of a magnetic field. This mixing results in a substantial modification of the structural parameters and physical properties of molecular systems. In particular, we observe a decrease in the saturated vapor pressure and an increase in the melting and boiling temperatures of the transition-metal hexafluorides.

For the Chevrel phases, the mixing of states of Van Vleck ions can be related to metallic properties. A change in the charge state in combination with a mixing of states of Van Vleck ions is the key element in the model of the singlemolecule switch based on a polynuclear metal cluster. It can also be assumed that the excitation of 'demagnetizing' orbital currents in anions (S^{2–} and so on) in Chevrel phases, which is due to the mixing of π^* and σ^* states in a magnetic field, is one of the factors responsible for the enhancement of critical magnetic fields in superconducting Chevrel phases.

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