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The Distribution of Spin Density in Paramagnetic Perovskite Crystals

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The distribution of spin density in crystals of the ABF_3 type with the perovskite structure ($A = Na^+$, Rb^+, Tl^+; $B = Mn^{2+}$, Ni^{2+}, Co^{2+}...) is recently intensively investigated with the NMR method (1,2,3). Our results of spin density f_s (per one bond with a magnetic ion) on the nuclei ^{19}F and ^{23}Na in $NaNiF_3$ can be compared with the f_s-values in $TlMnF_3$ and $RbMnF_3$ (Table 1). The f_s-value on the nucleus A depends essentially on the type of the paramagnetic ions B. The present paper deals with the theoretical explanation of this fact.

It shall be noted that with decreasing atomic distances in the row $TlMnF_3$-$NaNiF_3$ the spin density on the nucleus ^{19}F continuously increases. Besides, the f_s-value on the nucleus A in $RbMnF_3$ is greater than in $TlMnF_3$. Therefore one could expect that the f_s-value on the nucleus A in $NaNiF_3$ would be greater than in other crystals. However, no f_s-value has been found for ^{23}Na. The method of MO LCAO (4,5) may be

Table 1

The values of spin densities per one bond and the lattice parameters of the primitive cells

	T_N (°K)	Parameters of the cells (Å)	$(f_s)_F$ (%)	$(f_s)_A$ (%)
$TlMnF_3$ (1)	83	$a = 4.25$	0.51	- 0.030
$RbMnF_3$ (2,3)	83	$a = 4.14$	0.52	- 0.052
$NaNiF_3$	149	$\frac{c}{2} = 3.85$	0.56	0 ± 0.025

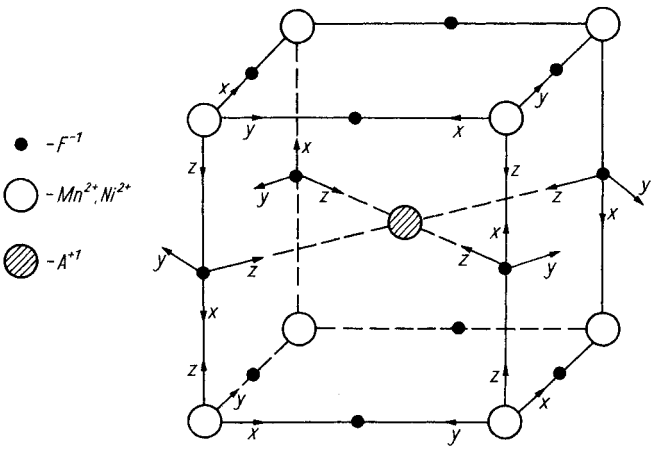

Fig. 1. The perovskite structure

used to analyse these experimental facts. We consider the complex AB_8F_{12} which has cubic symmetry. Fig. 1 shows the coordinate axes for each atom. The presence of a spin density on the nucleus of the ion A depends entirely on the polarization of s-orbitals as this ion has a cubic surrounding. Therefore we shall consider only MO which are invariants of the cubic group. We shall take into account 3d-orbitals of paramagnetic ions (d_{z^2}, $d_{x^2-y^2}$, d_{xz}, d_{xy}, d_{yz}) and 2p-orbitals of F (p_x, p_y, p_z). Using group theoretical methods (6) we find the possible invariant combinations of the previously mentioned AO. In our case only three exist:

$$\varphi_A = s\ ; \qquad \varphi_F = \frac{1}{\sqrt{12}} \sum_{i=1}^{12} p_z^i\ ;$$

$$\varphi_B = \frac{1}{\sqrt{24}} \sum_{j=1}^{8} \left(d_{xy}^j + d_{xz}^j + d_{yz}^j \right),$$

where the atoms F and B of a complex are denoted by the indices i and j, respectively. It is important that s does not belong to MO including d_{z^2} and $d_{x^2-y^2}$ AO of the atom B.

Analysing the cubic complex BA_8F_6 we get the same results. According to (1) we find three MO

$$\Phi_{antib} = N_1^{-1/2} \left[\varphi_A - (\alpha + S_{12}) \varphi_B + \gamma \varphi_F \right],$$

$$\Phi_{unb} = N_2^{-1/2} \left[- (\gamma + S_{13}) \varphi_A + \varphi_B - (\beta + S_{13}) \varphi_F \right],$$

$$\Phi_b = N_3^{-1/2} \left[\alpha \varphi_A + \beta \varphi_B + \varphi_F \right].$$

We assume that α, β, γ, and $S_{ik} \ll 1$. The spin density is due to the unpaired electron and the polarization of the filled orbitals by this electron. The d_{xy}, d_{xz}, d_{yz} orbitals of Ni^{2+}-ions wich have an octahedral surrounding are filled. It is natural to believe that the MO Φ_{unb} which consists mainly of this Ni^{2+} AO is also filled; therefore, in the first approximation no spin density exists upon the MO Φ_{unb}. In RbMnF where one electron is present per each d_{xy}, d_{xz}, d_{yz} orbital of Mn^{++}, there is one electron on Φ_{unb} and a spin density exists on the nucleus Rb. The f_s-value may be expressed as a function of the overlap integrals S_{ik} and the parameters of covelency α, β, γ, the latter depend on the direction of electron spin. In this case we have

$$(f_s)_{Rb} = \frac{1}{8} \left[\alpha_\uparrow^2 - \alpha_\downarrow^2 + (\gamma_\uparrow + S_{13})^2 \right].$$

This formula indicates that the spin density may be negative as well, which agrees with experiment (Table 1).

In this way the experimental results may be interpreted in the following manner: the nucleus A interacts with the d_{xy}, d_{xz}, d_{yz} orbitals of the ion B. If unpaired electrons are present on these orbitals, a spin density exists on the nucleus A. Otherwise, there is no spin density on the nucleus A.

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