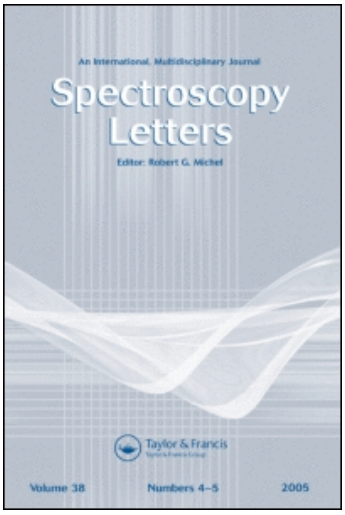

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Magnetic Screening of ^{19}F Nuclei in Perovskite $KMgF_3$

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MAGNETIC SCREENING OF ^{19}F NUCLEI IN PEROVSKITE $KMgF_3$

KEY WORDS: metal fluorides, fluorine NMR chemical shift

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The present work cites the measurement data for the magnetic screening tensor of fluorine nuclei in $KMgF_3$ and comparison results of ^{19}F screening tensor components in this substance with the theoretical, based on the overlapping pattern of ion wave functions.

$KMgF_3$ samples approximately 1 cc in size were grown from melt. Orientation of the samples was performed in accord with the external shape and controlled with the aid of an X-ray goniometer.

^{19}F NMR spectra were recorded in fields up to 9 and 23.5 kOe on JNM-3H-60 and JNM-4H-100 spectrometers respectively. ^{19}F NMR chemical shifts were determined by the shift magnitude of the signal gravity centers in relation to the liquid CCl_3F signa l (for which the shift in relation to F_2 is known[1] to equal 421.10^{-6}). Procedure[2], eliminating whatever errors arising on account of the phase detector constant, was used. Dispersion admixture in the spectra was practically imperceptible. The screening anisotropy magnitude was estimated from the dependence of the spectra second moments on the external magnetic field stress.

$KMgF_3$ crystals belong to the cubic syngony, and at 300°K $a_o = 4.00$ Å. Mg-ions are situated in the cubic elementary cell centers, K-ions in the apices, and F-ions in the face centers.

It was found that with crystal rotation about the [001] axis the NMR spectra do not show marked asymmetry, and the shift of the spectra maxima does not depend on orientation and is $(197 \pm 10).10^{-6}$ in the high field direction with respect to the CCl_3F signal.

In accord with the $KMgF_3$ structure, at external field orientation along direction [100], there are two ^{19}F nuclei positions, nonequivalent in relation to the magnetic field. For one of these the F-Mg bonds are parallel to [100], while for the other they are perpendicular; the number of nuclei in the latter position is twice that in the first. Inasmuch as $KMgF_3$ possesses cubic symmetry, and the F-ions are situated on the four-fold axis, the screening tensor is symmetrical to the axis. In this case the σ_p may be represented as:

$$\sigma_p = \bar{\sigma} + \Delta\sigma(3\cos^2\theta - 1),$$

where θ is the angle between direction H_o and the screening tensor axis.

The main tensor axis should coincide with the direction of the Mg-F bonds (i.e. the direction of the crystal four-fold axes). Hence, with H parallel to [100], the NMR spectrum, dipole-dipole interaction not taken into consideration, should present a doublet with a split equal to $3\Delta\sigma$ and a 1:2 doublet component intensity ratio. Since the experimental spectrum does not show neither doublet split, nor asymmetry, one must assume that the $\Delta\sigma$ value is small. For evaluating the possible

higher limit for the experimental $\Delta\sigma$ value, the dependence of ^{19}F NMR spectra second moments on the applied field magnitude, orientated parallel to [100], was scrutinized. The S_2-on-H_o dependence may be represented as[3]:

$$S_2 = S_2^o + 2(\Delta\sigma H_o)^2,$$

where S_2^o is the ^{19}F NMR spectrum second moment value with H_o approaching zero. This value is determined both experimentally and theoretically by using Van Fleck's formula for calculating the already known structure.

Fig. 1 shows the dependence of ^{19}F NMR spectra second moments in $KMgF_3$ upon the applied field in the 3 to 23.5 kOe range. It is apparent that the experimental values within the entire range coincide with S_2^o = 6.45 Oe^2, calculated by means of Van Fleck's formula, and, for this reason, the higher limit $\Delta\sigma$ is determined with the value of experimental scattering of S_2 in the 23.5 kOe field, amounting to about 5%. The possible value of $\Delta\sigma$, obtained herewith, is less than 10^{-5}. Hence, $\Delta\sigma = (0 \pm 10)10^{-6}$.

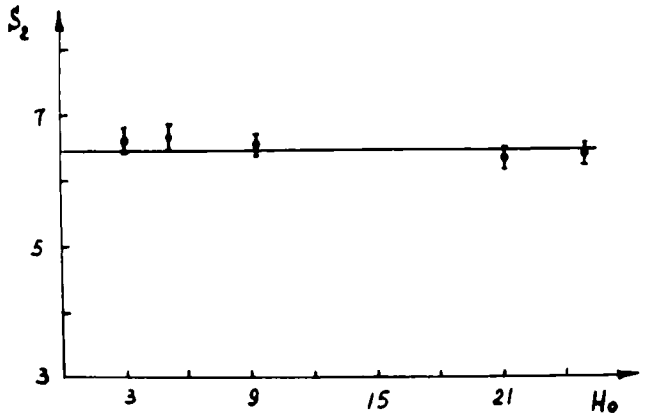

FIG. 1

The dependence of ^{19}F NMR spectra second moments S_2 in $KMgF_3$ upon the applied field.

Thus, notwithstanding the anysotropic character of the fluorine surroundings in $KMgF_3$ (each F-ion is surrounded by two Mg- and four K-ions respectively), the F-ion electron cloud possesses practically cubic symmetry. At first sight this result appears wholly unexpected and requires explanation arising from the peculiarities of the F-M and F-K bonds.

At present it is considered established that magnetic screening of nuclei in ion crystals is mainly due to the overlapping of ion wave functions.[4,5] According to this viewpoint, the screening constant diamagnetic and paramagnetic parts are expressed through the overlap-integrals.

Löwdin's method[6] was used for calculating the overlap-integrals, and the Hartry-Fock[7,8] equation solutions were taken as the wave function radial parts. Numeric calculations were chiefly performed with Simpson's formula. The F-F and F-K overlap-integrals were taken from work[9]. The table below cites the overlap-integral values essential for finding σ_p.

TABLE

Bond	Interionic distance	$S(2p\sigma \mid np\sigma)$	$S(2p\sigma \mid ns)$	$S(2p\pi \mid np\pi)$
F-Mg	2.00 Å	- 0.0466	0.0598	0.0287
F-K	2.82 Å	0.0595	0.0470	- 0.0149
F-F	2.82 Å	0.0715	- 0.0410	0.0233

The screening constant diamagnetic part alteration, caused by atom orbital overlapping, equals approximately 1.10^{-6}, and the input of the said diamagnetic part into the chemical shift may be ignored.

Assuming ΔE - the fluorine 2p-electron mean excitation energy equal to 10 eV, the following values are obtained: $\sigma_{\parallel} = -129.3 \cdot 10^{-6}$, $\sigma_{\perp} = -128 \cdot 10^{-6}$, $\bar{\sigma} = \frac{1}{3}(2\sigma_{\perp} + \sigma_{\parallel}) = -128.4 \cdot 10^{-6}$, $\Delta\sigma = 0.33 \cdot 10^{-6}$ and $\eta = 0$. If the value of the F_2 chemical shift with respect to the fluorine free ion is taken[10] as $-717 \cdot 10^{-6}$, then $\bar{\sigma} = 589 \cdot 10^{-6}$, which coincides with the experimental $\sigma = (618 \pm 10)10^{-6}$. In this case $\sigma_{\parallel}$ is the ^{19}F σ_p value when the field is along the F-Mg bond, and $\sigma_{\perp}$ is the field perpendicular to the bond. The small $\Delta\sigma$ value in $KMgF_3$ is due to the proximity of the F-Mg and F-K overlap-integral values. Thus, the Kondo-Yamashita model, based on the assumption of the ionic nature of the bond in the crystal, is in sound accord with experiment (not only for $\bar{\sigma}$, but for $\Delta\sigma$ likewise) on presuming that there is an orbital overlapping of fluorine with the orbitals of all the neighboring ions.

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