Systematic Investigation of MF_3 Crystalline Compounds ($M = Al, Cr, Fe, Ga, In, Sc, Ti, and V$) and $Fe_{1-x}M_xF_3$ Mixed Series ($M = Ga, Cr, V$) *

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The electric field gradient at the fluorine site of several crystalline trifluorides was measured by means of the time differential perturbed angular distribution method. The hyperfine data (ν_Q and η) are systematically analyzed by taking into account the structural parameters of the crystals; they are also compared to the results obtained by point charge calculations.

Introduction

During the last fifteen years, the intrinsic character of the fluorine ion, mainly its low polarizability, evoked much fundamental interest in the physical properties of fluorides. In the case of iron based fluorides, the electric field gradient (EFG) at the ^{57}Fe sites was determined by Mössbauer spectroscopy [1]. On the other hand, the time differential perturbed angular distribution (TDPAD) technique can provide EFG data at the ^{19}F site. This motivated the present studies on MF_3 crystalline compounds.

With M = Al, Cr, Fe, Ga, Ti and V, these trifluorides crystallize at high temperatures in the Pm3m space group. The lattice is built up from a cubic network of corner sharing MF_6 octahedra. By cooling below the structural transition temperature T_c, a tilting of the MF_6 octahedra by an angle ω_n around one three fold axis of the cubes occurs, inducing a rhombohedral distortion of the structure; in this phase the space group is $R\bar{3}c$. In all these compounds T_c is above the room temperature. On the other hand, the crystallographic data are not so clear in the case of Sc and In trifluorides: different structures are proposed in the literature: rhombohedral [2], hexagonal-rhombohedral [3] and cubic [4] for ScF_3 and rhombohedral or monoclinic for InF_3. These aspects are relevant for the discussion of experimental data, but the TDPAD hyperfine parameters are not highly sensitive to symmetry conditions.

After a brief description of the experimental aspects, the results of the measurements are reported. The hyperfine data are discussed in terms of the electronic configuration and structural parameters. In order to model the EFG at the ^{19}F site, point charge calculations were performed and compared with the experimental data.

Also experiments on mixed ferric crystals are presented and discussed in the perspective of amorphous fluorides. As a matter of fact, special attention is actually focused on mixed ferric series such as $Fe_{1-x}M_xF_3$ (M = Ga, Cr and V) because of their magnetic properties. These compounds crystallize in the space group $R\bar{3}c$ at room temperature, identically to that of the pure MF_3 compounds. Mössbauer and susceptibility measurements have recently revealed various magnetic properties, such as reentrance phenomena, spin clustering and weak anti-ferromagnetism, essentially originating from the cationic disorder [5]. In the case of amorphous trifluorides (a-FeF_3, a-GaF_3, a-AlF_3), numerous structural and magnetic studies were motivated due to the topological disorder. EFG calculations were applied on structural networks based on a continuous random dense packing of corner sharing

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octahedra, using a point charge model. In spite of the rather complex structure, ^{57}Fe in-field Mössbauer experiments have provided experimental EFG distributions which are in agreement with the calculated ones [6]. For these reasons, the TDPAD experiments were extended to these systems.

Experimental

The ^{19}F-TDPAD experiments were done by means of a 5 MeV pulsed proton beam, populating the second excited F-level via inelastic $^{19}F(p, p')^{19}F^*$ scattering. The experiments on MF_3 (M = Al, Cr, Ga, Sc, Ti, Sc) and $Fe_{1-x}M_xF_3$ ($0 < x < 1$, M = Ga, Cr, V) were carried out at room temperature, whereas the ferric trifluoride was studied at temperatures from 360 K to 530 K; the Neél temperature is $T_N = 363$ K. Since the experiments were carried out on powder samples, the random orientation of the micro crystals smears out the modulation pattern caused by the electric and magnetic hyperfine interaction, for T below T_N.

Results and Discussion

In the case of FeF_3, the temperature dependence of the hyperfine parameters was studied in the paramagnetic range. As illustrated in Fig. 1, the interaction amplitude is continuously decreasing when T_N is approached from above, and is constant for T above T_N. This can be interpreted as an increasing amount of short range magnetic ordering probed at the fluorine site when the temperature decreases towards T_N.

In Fig. 2 some typical TDPAD spectra for the investigated pure compounds are shown, whereas the corresponding hyperfine data are given in Table 1 together with some structural parameters. Strong correlations are observed between the hyperfine and the crystallographic parameters: one example is given in Fig. 3, where the tilt angle ω_n is plotted versus the asymmetry parameter η. The correlations hold quite well for M = Ga, Fe, Cr, V, Ti, and Sc, whereas considerable deviations occur for Al and In. This may be due to the different electronic structures of Al and In compared to the other cations. Al, as period 3 element, has no d electrons, whereas In is a period 5 element: so the 4d shell is the relevant electron shell compared to the 3d shell in the other cases. Further contributions are due to the above doubts concerning the crystallographic structure. The observed trends for the remaining compounds can be well understood: (i) the asymmetry parameter increases with ω_n in agreement with the progressive distortion of the axial symmetry of the EFG at the fluorine site, (ii) the decrease of the quadrupole coupling constant ν_Q is correlated to the increasing M–F-distances and ionic radii.

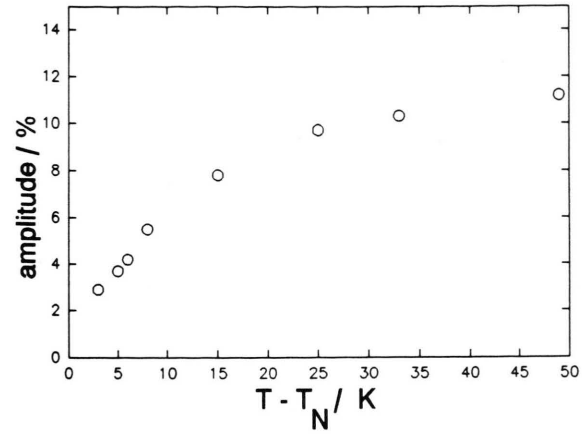
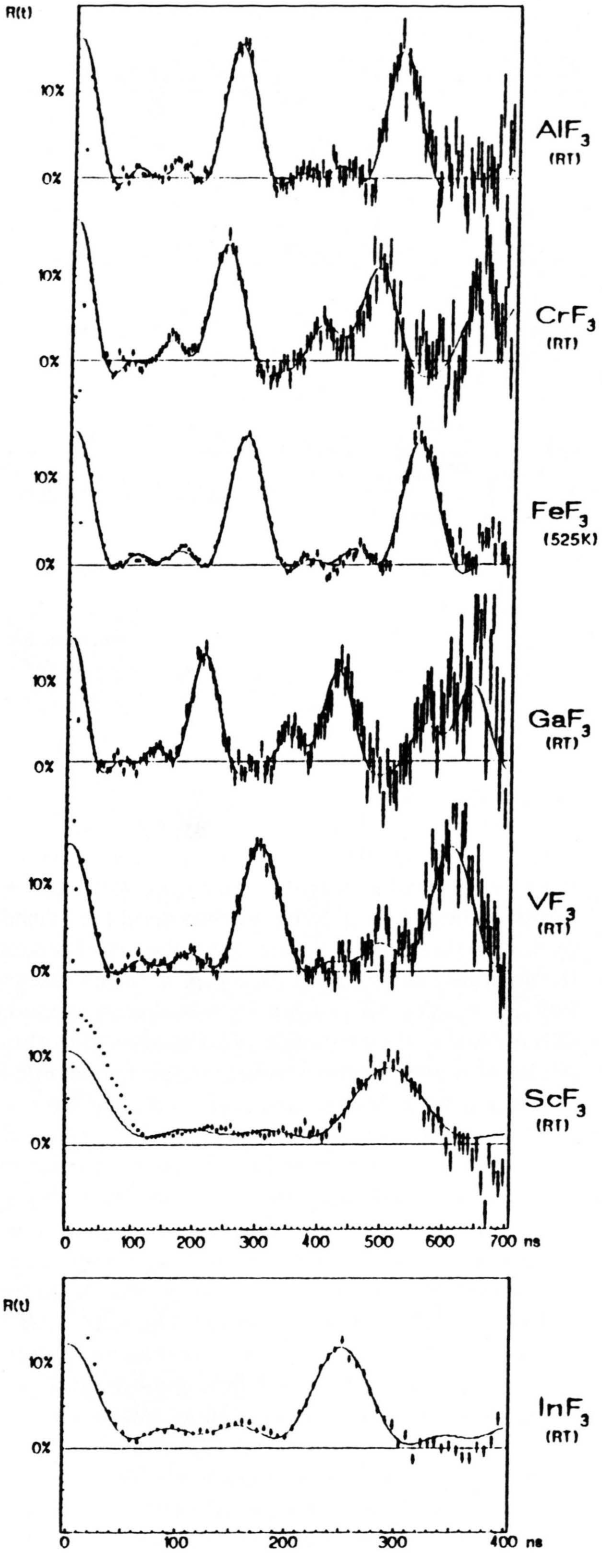


Fig. 1. Variation of the observed hyperfine interaction amplitude in FeF_3 with temperature.

Besides hyperfine and geometrical correlations, the electronic configuration determined by the number of 3d electrons can also be considered, as shown in Figure 4. Going from scandium to chromium the 3d shell is successively filled with electrons according to Hund's rule, and the ionic radii decrease with increasing atomic number. However, for Fe there exists the possibility of either a low-spin or a high-spin configuration of the electrons. For the low-spin configuration the trend of decreasing radii with increasing atomic number is continued, whereas for the high-spin configuration a considerably higher radius occurs and the trend is broken (Figure 4a). In Fig. 4b the observed values for ν_Q are plotted versus the corresponding number of 3d electrons. For Sc to Cr, with increasing number of 3d electrons and corresponding decrease of ionic radius the observed ν_Q values increase. If Fe^{3+} were in the low-spin configuration, according to the trend a value of approximately 32 MHz could be expected for the quadrupole coupling constant. However, the experimental value is 24 MHz. Consequently, the configuration of Fe^{3+} in FeF_3 can be identified as the high-spin configuration, in accordance with other methods, for example ^{57}Fe-



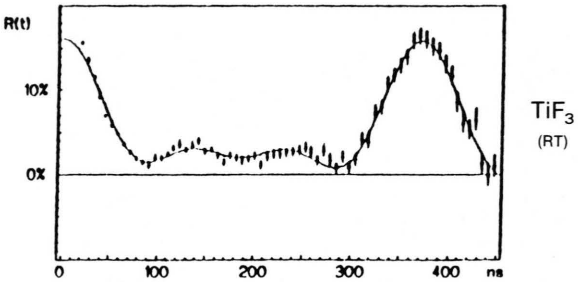


Fig. 2. Typical $R(t)$-spectra for AlF_3, CrF_3, FeF_3, GaF_3, VF_3, ScF_3, InF_3, and TiF_3. All spectra are obtained at room temperature (RT) except for FeF_3 where $T = 525$ K.

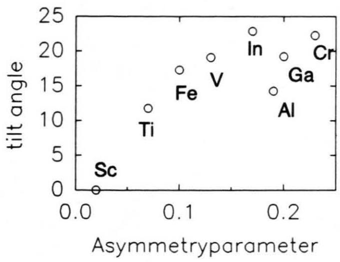


Fig. 3. Correlation between ω_n and η. Increasing ω_n corresponds to increasing deviation from axial symmetry of the fluorine lattice site and therefore to increasing η.

Table 1. Observed hyperfine parameters together with some structural data for the investigated MF_3 compounds.

Comp.	ν_Q/MHz	A_{22}/%	η	ω_n/°	r_M/Å	α/°
ScF_3	13.8	7.9	<0.02	0	0.745	59.53
TiF_3	17.7	16.8	<0.07	11.76	0.670	59.07
FeF_3	24.0	14.5	0.10	17.29	0.645	57.99
VF_3	21.6	14.5	0.13	19.08	0.640	57.52
InF_3	25.8	12.0	0.17	22.82	0.790	56.35
AlF_3	25.5	15.5	0.19	14.26	0.535	58.62
GaF_3	30.7	15.5	0.20	19.22	0.620	57.50
CrF_3	27.1	16.2	0.23	22.22	0.615	56.56

For InF_3 and ScF_3 the structural data are given for the reported rhombohedral phases.

Mössbauer experiments at the iron site. The same systematics occur for the asymmetry parameter η. In principle the same behaviour could be observed for MnF_3 ($\nu_Q = 28.5$ MHz), but in this case the splitting of the radii between the low-spin and the high-spin configurations is much smaller. A strong Jahn-Teller effect is expected in this compound, and the crystal structure is not rhombohedral but monoclinic. Therefore the systematics can be applied only to the quadrupole coupling constant.

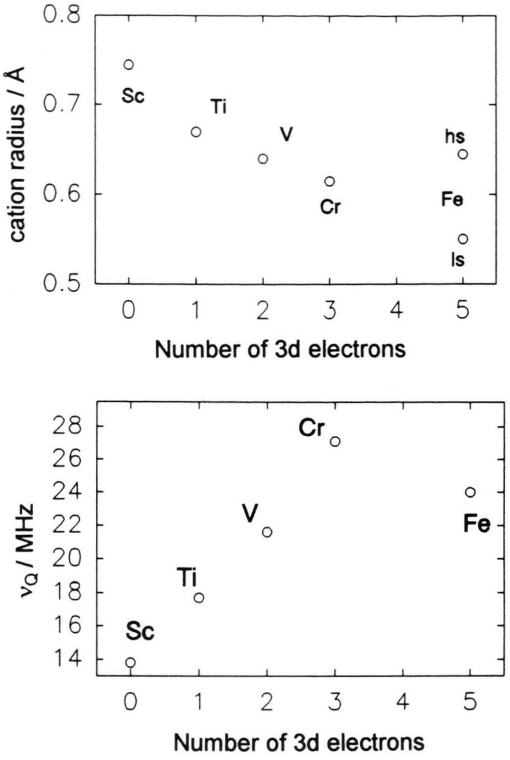


Fig. 4. Variation of ionic radii (a) and EFG-values (b) with the number of 3d electrons.

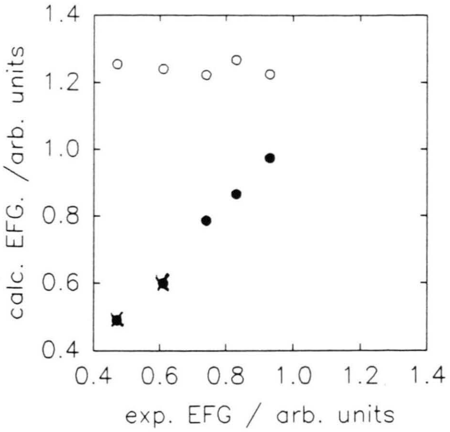


Fig. 5. Plot of calculated EFG's vs. observed ones: o calculation with full charges; ● calculation with reduced charges according to Daniel et al. [8]; ✱ calculation with predicted valued for reduced charges.

Table 2. Compilation of the reduction factors for the charges.

M^{3+}	Red. factor	Ref.
Sc^{3+}	0.4	this work
Ti^{3+}	0.6	this work
V^{3+}	0.665	[8]
Cr^{3+}	0.795	[8]
Fe^{3+}	0.683	[8]

Results of EFG Calculations

EFG calculations using a point charge model were applied to the MF_3 structures for M = Sc, Ti, V, Cr, Fe. In the used algorithm the crystalline lattice is built up from shells of unit cells with splitted ions at corners, edges and faces in order to get structural units with zero monopolar and dipolar moments. Calculations were done in direct space for up to seven shells, and the convergence of the EFG parameters was controlled by means of a Neville's plot. After calculating the monopolar contributions, the effect of dipoles at the lattice sites, induced by the field of the charges, was obtained by a self consistent procedure. More details about these calculations are given in [7].

It turned out that a nice agreement between experiment and calculation could be achieved for the values of the asymmetry parameter η when the charges of the cations were set to $+3$ and those of the anions to -1. On the contrary, a large disagreement is observed for the quadrupole coupling constant itself, as shown in Fig. 5, where the calculated values are plotted against the observed ones. A good agreement with experiments for both hyperfine parameters can be obtained by using a set of reduced charges for the ions, keeping the neutrality condition $Q_M + 3Q_F = 0$. In the case of FeF_3, CrF_3, and VF_3 such a set was already successfully applied to the evaluation of lattice dynamics data [8]. In these experiments the Raman spectra recorded at room temperature can be well described from a rigid ion model based on the superposition of short range interatomic forces and coulombian ionic interactions. The calculation procedure consists in fitting the Raman line positions, assuming free force constants and effective charges; this leads to a set of reduced charges whose values are very close to those deducable from the TDPAD results. This effect is due to the similarity of the analytic development in both lattice dynamics and electric field gradient calculations. Consequently, reduced charge values can be predicted for the other MF_3 compounds (Table 2) due to the confidence of the present calculations. This reduction can, at least in part be attributed to the partially covalent character even of the ionic compounds,

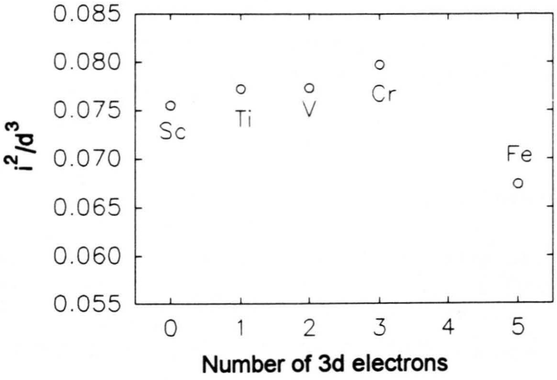


Fig. 6. Lot of i^2/d^3 vs. number of 3 d electrons.

as stated a long time ago by Greenwood [9], however no numerical values were given. It must also be stressed that by no means the reduced charges used to adapt the point charge calculations to the experimental results may be interpreted in terms of real charges located at the lattice sites of the corresponding ions. In the contrary, when passing in the periodic table from Sc to the right, the electronegativity difference $\Delta\chi$ to fluorine decreases, resulting in decreasing ionicity *i*. The corresponding *i* values lie between 83% and 70% according to the relation $i = \exp(-0.25\,\Delta\chi^2)$ [10]. This quantity *i* may be interpreted in terms of a real charge leading to decreasing charges from Sc to Cr. In the calculations there is some kind of selfcompensation: for the distances in the point charge algorithm the experimentally observed ones are used. These quantities, however, are already reduced by covalency effects and give therefore raise to higher calculated EFG values. This can easily be demonstrated when plotting the term i^2/d^3 (d: M–F-distance) versus the number of 3 d electrons. In Fig. 6 an increase of i^2/d^3 versus the number of 3 d electrons, except for Fe, is observed.

So the reduced charges may be interpreted as a combination of the described selfcompensation effect and ionicity *i* on one hand, and by a kind of "formfactor" on the other hand. This formfactor takes into account, by a scalar value, the deviation of the real 3-dimensional ions from the 0-dimensional point objects used for the calculations.

In an earlier paper [11] a correlation between the number of 3 d electrons and observed ν_Q-values was also established, however the discussion did neither take into account any details of the crystal structure nor was there an explanation for the discrepancy between the experimental and the observed data.

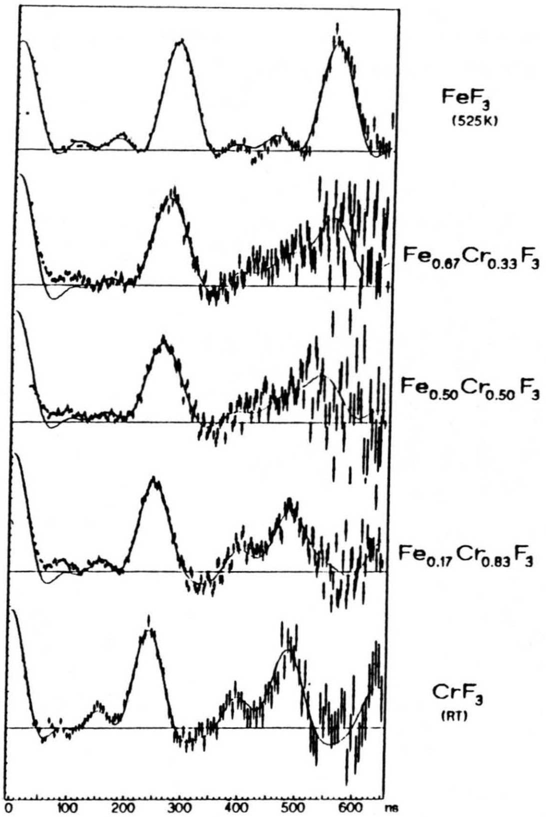


Fig. 7. $R(t)$-spectra for mixed ferric compound $Fe_{1-x}M_xF_3$ at room temperature.

In Fig. 7 the first preliminary $R(t)$-spectra recorded on $Fe_{1-x}Cr_xF_3$ are shown. A well pronounced modulation can clearly be seen, which gradually changes from the pure FeF_3 pattern for $x = 0$ to the pure CrF_3 one for $x = 1$. However the main differences in the spectra occur above 500 ns, where unfortunately in the present spectra the statistics are poor. For $0 \leq x \leq 1$, the spectra can be well reproduced either by fitting a single coupling constant varying between 24 MHz and 27 MHz, or by two coupling constants of approximately 24 MHz and 27 MHz with x-dependent relative amplitudes. However, even the presence of the observed well pronounced modulation is promising for future experiments which will be carried out with improved statistics. As explained above, the magnetic behaviour of these mixed compounds is one source of the specific interest in them. For that reason there will be also temperature dependent experiments on the $Fe_{1-x}V_xF_3$-compounds. In these compounds, the paramagnetic phase transforms via a phase for

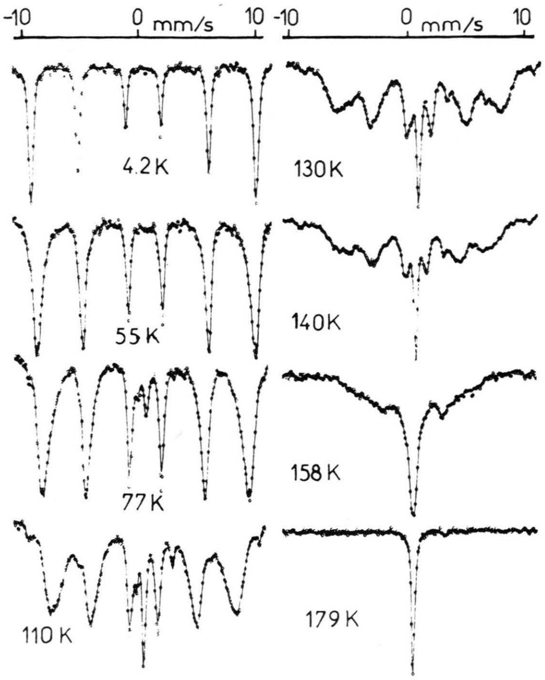


Fig. 8. Mössbauer spectra for $Fe_{0.5}V_{0.5}F_3$ recorded at given temperatures [12]. The transformation of the paramagnetic single line spectrum at high temperatures to the low-temperature magnetic sextett via a region where the spectra consist of a superposition of a singulet and a magneic sextett can clearly be observed.

which paramagnetism and magnetic order coexist (Figure 8). This coexistance is extended over a range of about 100 K [12].

Conclusions

The experiments and calculations on MF_3 crystalline compounds and the first results for the mixed ferric fluorides are very promising: the agreement of the calculated EFG data requires reduced charges in harmony with lattice dynamics; and also in the compounds which are governed by cationic disorder, well pronounced TDPAD spectra can be observed. Therefore the present work represents a first step to further investigations of mixed crystalline fluorides and amorphous systems.

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