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On the charge compensation effects in Mn(II) doped $(NH_4)_2SbF_5$: EPR study

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Electron paramagnetic resonance of Mn(II) ion doped in bis (ammonium) pentafluorostibnate is reported. Local charge compensation is proposed as the reason for the doubling of the expected single site. A $\pm 20°$ rotation of the MnF_5^{3-} moeity about the crystallographic a axis has been attributed to charge compensation processes. The D tensor is found to have the values $D_{zz} = 0.0358$ cm^{-1}, $D_{yy} = -0.028\,62$ cm^{-1}, $D_{xx} = -0.007\,26$ cm^{-1}; the Mn hyperfine coupling is found to be -0.0095 cm^{-1}. The apical flourine does not give resolved hyperfine coupling, while the four basal flourine atoms give hyperfine couplings in the range $a_{max} = 0.0018$ cm^{-1}, $a_{min} = 0.0015$ cm^{-1}.

INTRODUCTION

High spin Mn(II) is probably the most studied of the transition metal ions. Many excellent review articles on the EPR of Mn(II) have appeared in the literature.[1-3]

Manganese generally forms poor covalent bonds and information regarding ligand superhyperfine interaction is seldom available. Still the single crystal EPR of high spin Mn(II) has attracted the attention of many researchers for the following reasons:

(1) Being an S-state ion characterized by long T_1 (spin-lattice relaxation) Mn(II) gives well resolved ESR spectra at room temperature and even at high temperatures.

(2) The zero-field tensor is extremely sensitive to the symmetry of the crystal field environment. For example, the cubic field symmetry of MgO,[4] CaF_2,[4,5] ZnS,[6,7] and Cd(imidazole)$_6$(NO$_3$)$_2$[8] is clearly understood by single crystal EPR studies of such systems with Mn(II) as a probe. Their spectra show only a cubic variation with magnetic field.

The EPR of Mn(II) with fluorides as ligands has been reported by many authors. Most of these hosts are alkali or alkaline earth fluorides where Mn(II) is coordinated octahedrally or cubically.[9,10] Our motivation is to study EPR of Mn(II) in a square pyramidal environment of fluorines and $(NH_4)_2SbF_5$ is chosen as a suitable host. In this lattice Sb^{3+} ion may be replaced by Mn^{2+} to get square pyramidal MnF_5^{3-}. But charge compensation should occur due to charge difference. This may take place locally, in which case the magnetic parameters are affected, or the charge compensation may take place sufficiently away from the impurity such that the magnetic parameters are not affected.

EXPERIMENTAL

Single crystals of $(NH_4)_2SbF_5$ were obtained by dissolving SbF_3 and NH_4F in the molar ratio 1:3 in 40% HF. Mn(II) (about 1%) was added in the form of MnF_2. Good single crystals with well developed faces were obtained in a few days. The crystal morphology is given in Fig. 1. The morphology was determined on a Enraf Nonius CAD-4 x-ray diffractometer. Selected single crystals were rotated both in the X-band and in the Q-band spectrometers about the crys-tallographic a, b, and c axes. Spectra were recorded for every 10° interval.

$(NH_4)_2SbF_5$ belongs to orthorhombic system with space group $Cmcm$ with the unit cell parameters $a = 6.497$, $b = 14.162$, $c = 6.772$ Å, $Z = 4$.[11] Only one magnetically distinct site is expected in the absence of charge compensation effects. The projection of the unit cell along the crystallographic a axis is shown in Fig. 2. The relation between molecular geometry and crystallographic axes is shown in Fig. 3.

X-band measurements were made in the Varian E-4 spectrometer and Q-band measurements in the Varian E-112 EPR spectrometer. Measurements at 77 K were carried out at X-band by immersing the mounted crystal in a quartz Dewar vessel whose tail fitted in the Varian E-231 multipurpose cavity.
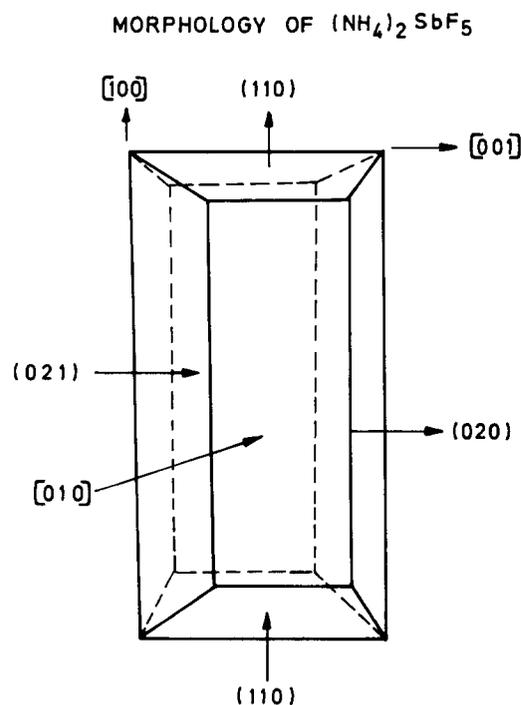
MORPHOLOGY OF $(NH_4)_2 SbF_5$

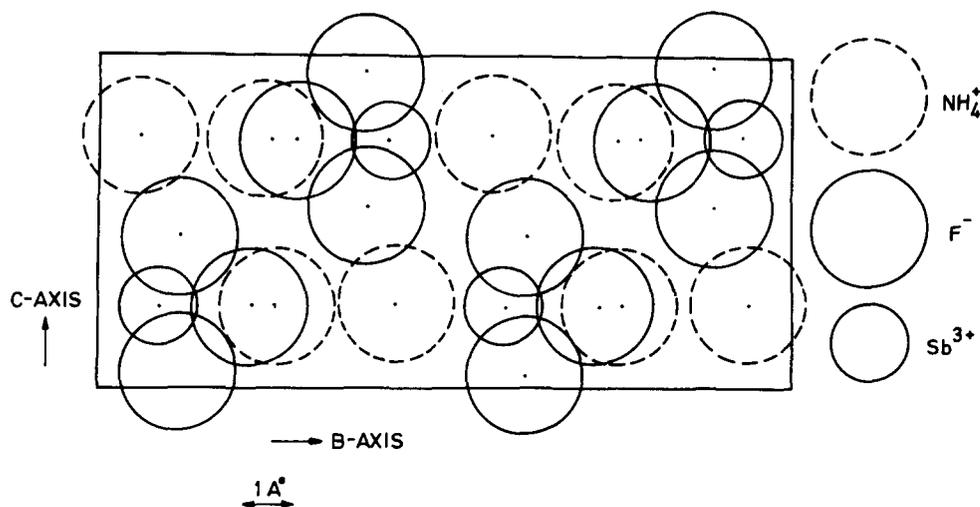FIG. 1. Morphology of the single crystal of $(NH_4)_2SbF_5$.

FIG. 2. Projection of the unit cell of $(NH_4)_2SbF_5$ along the crystallographic a axis.

RESULTS AND DISCUSSION

At both X-band and Q-band frequencies the spectra were essentially the same except that second order effects were less noticeable at Q-band frequency. At any arbitrary orientation, the spectrum consists of two sets of 30 lines corresponding to $I = 5/2$ and $S = 5/2$ (of Mn^{2+}) and each of these 30 lines, at most orientations is split into a quintet of relative intensity 1:4:6:4:1, obviously due to superhyperfine interaction with four fluorine ligands $(I = 1/2, 100\%)$. Therefore, there are two spatially distinct sites of MnF_5^{3-} per unit cell. The EPR spectrum for magnetic field close to D_{zz} axis is shown in Fig. 4. From the projection of the host SbF_5^{2-} units it is expected, since all SbF_5^{2-} units are magnetically equivalent, there can only be a single paramagnetic site for Mn(II) ion. It is also expected that the principal axes of D tensor will coincide with the three Cartesian axes of SbF_5^{2-} pyramid with D_{zz} parallel to the C_4 axis and D_{xx} and D_{yy} being bisectors of the F–Sb–F bond in the basal plane. In fact for Fe(III) in this host, the D tensor was found to be nearly axially symmetric (E is very small) and the principal axes coincide with the crystallographic axes.[12] In the present case, however, the following important features were found.

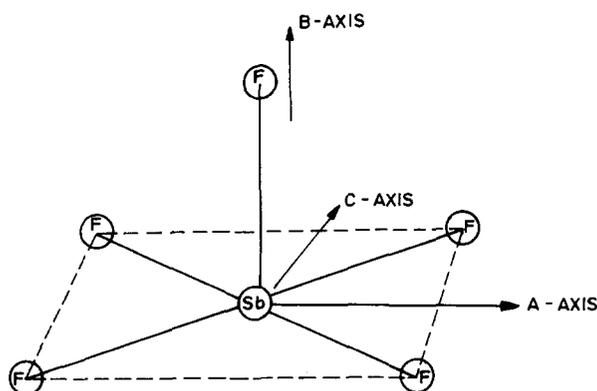(1) The D tensor was highly orthorhombic with a large E factor.

FIG. 3. Schematic diagram which shows the relation between the crystallographic axes and the Sb–F bonds in $(NH_4)_2SbF_5$.

(2) For rotation about the crystallographic b and c axes these sites coincide throughout, while for a axis rotation there were two distinct sites with identical angular variation with a phase difference of $\pm 20°$ about the crystallographic b axis.

In order to derive the principal values of the D tensor we have used a diagonalization procedure similar to the one used for g and hyperfine tensors. These were further refined by setting the spin Hamiltonian

$$\mathscr{H} = g\beta HS + D\left[\tfrac{1}{3}S_z^2 - S^2\right] + E\left[S_x^2 - S_y^2\right],$$

ignoring the nearly isotropic ^{55}Mn hyperfine and ^{19}F ligand hyperfine structures, where g was isotropic at 2.0036, and D and E were varied using a tetrahedral interpolation procedure of Kopp.[13] The angular variation of the centroid of the five sets of sextets, both experimental and calculated from an exact diagonalization of spin Hamiltonian with the best fitted D and E, for rotation about crystallographic a and c axes, are given in Figs. 5(a) and 5(b). It can be seen that the agreement is excellent. The magnetic parameters are given in Table I. The fluorine hyperfine coupling was not followed throughout, since at many orientations the resolution was poor. However, an estimate of the upper and lower values was made and these are also given in Table I.

The presence of two magnetically distinct sites can only be explained by a superposition of a low symmetry distortion brought about by a charge compensating influence. This may be a nearest neighbor fluorine ion vacancy or the presence of an interestical NH_4^+ ion. From the observed results it is evident that the charge compensating vacancy must be close to Mn(II) to result in a highly orthorhombic D tensor.

From an examination of positional parameters of near-neighbor fluoride ions it was found that there is no fluoride ion that is not already involved in coordination with Mn(II) within 5 Å. From the absence of superhyperfine interaction from the apical flourine, one might be tempted to propose that Mn(II) enters as MnF_4^{2-} square planar or tetrahedral moeity. However, this can be easily ruled out as follows. Square planar MnF_4^{2-} is thermodynamically unstable and even if it were stable, since all Mn–F bonds are situated in the ac plane of the crystal, this would not lead to splitting of sites into two. Tetrahedral MnF_4^{2-} is not expected to have such a
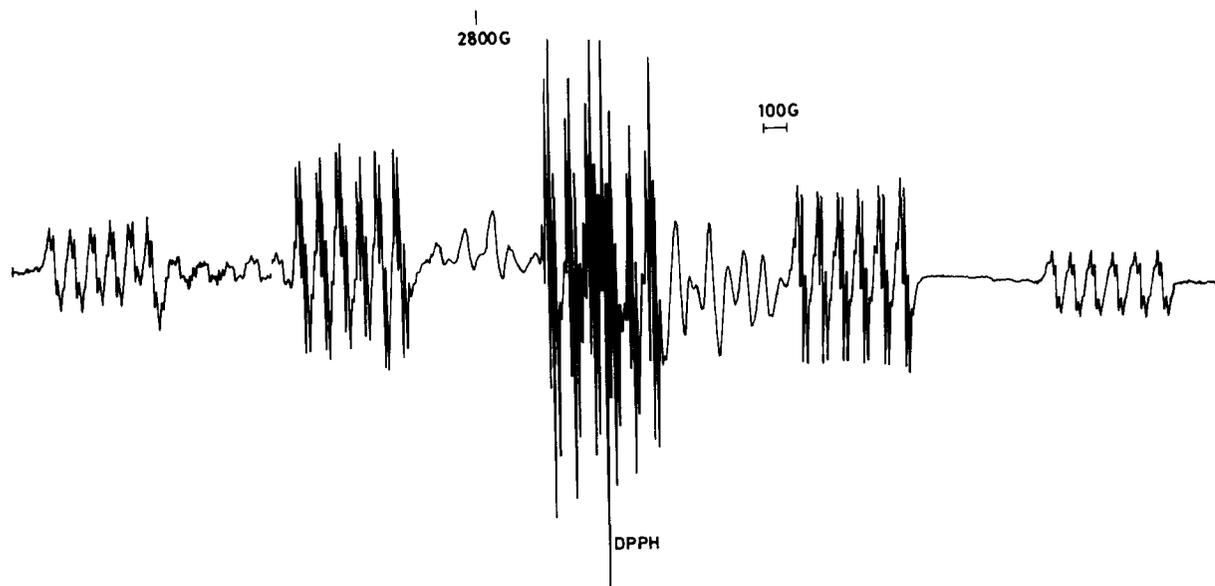
FIG. 4. EPR spectrum of Mn(II) in $(NH_4)_2SbF_5$ when the magnetic field is close to D_{zz} for one of the two sites.

highly orthorhombic D tensor. In this case also the presence of two sites cannot be explained. Charge compensation therefore must come about by the presence of an NH_4^+ ion in next-neighbor interstetial location. It was found on examining the lattice, that two of the flouride ions ligated to a given Mn(II) and two other fluorines belonging to a neighbor SbF_5 unit form a parallelogram, the center of which is sufficiently wide to accommodate the NH_4^+ ion. It is now necessary to postulate that the introduction of NH_4^+ ion at the abovementioned site should rotate MnF_5^{3-} units about the crystallographic a axis by $\pm 20°$, in order to explain the observed orientation of the D tensor and the two magnetically distinct sites.

A CNDO/2[14] calculation was carried out wherein a Na^+ (to simulate the isoelectronic NH_4^+ ion) was incorporated in the abovementioned F_4 parallelogram, the MnF_5^{3-} unit and the next neighbor SbF_5 unit were rotated about the crystallographic a axis (see Fig. 6). The rotation was performed both in clockwise and anticlockwise direction depending on the location of the neighbor SbF_5 unit relative to the MnF_5^{3-} moeity. The introduction of sodium itself reduced the energy by 0.3 a.u.; further reduction in energy occurred with a minimum for a rotation about the a axis by $\pm 30°$ from the crystallographic b axis. It is therefore quite reasonable that the actual experimental value is $\pm 20°$ as a result of this charge compensating vacancy, considering that we have incorporated a limited set of lattice points. As such it is concluded that the presence of a charge compensating unipositive ion which is most likely NH_4^+, does produce a local twisting of the MnF_5 either by $+20°$ or $-20°$ about the crystallographic a axis giving rise to the observed two sites. D_{zz} is still controlled by the Mn–F (apical) direction and at the same time the presence of NH_4^+ ion introduces additional anisotropy in the D_{xx}, D_{yy} plane leading to a large E. Cooling the system to 77 K did not alter the spectra.

The relative sign of D and A manifest themselves by difference in the hyperfine coupling measured from the low field and the high field sextets.[15] If D and A are of the same sign, the mean hyperfine separation would be greater in the low field sextet than the high field one and vice versa. This is because the second order effects, which produce a variation in the spacing of hyperfine component in the different electronic transition, follow the equation for the energy of transition given below:

$$h = G + Am\left\{1 + \left(\frac{A_{\parallel}A_{\perp}^2}{2A^2G}\right)(2M-1)\right\}$$
$$+ (A_{\parallel}^2 + A_{\perp}^2)\left(\frac{A_{\perp}^2}{4A^2G}\right)[I(I+1) - m^2]$$
$$+ \left[\frac{(A_{\parallel}^2 - A_{\perp}^2)^2}{8A^2G}(g_{\parallel}^2 g_{\perp}^2/g^2)^2\sin^2 2\theta\right]m^2,$$

where $G = g\beta H$.

With magnetic field parallel to D_{zz}, the low field separation for one of the two sites of Mn(II) is 92.5 G, while the separation at high field is 96.25 G indicating A and D are of opposite sign. Since A is invariably negative being due to core polarization of inner orbitals for high spin Mn(II), it may safely be inferred that the sign D for Mn(II) in $(NH_4)_2SbF_5$ is positive.

It is possible to calculate the covalency of the bonds in MnF_5 moeity using Matumura's plot,[10] the following relation is used to calculate the covalency:

$$C = \frac{1}{3}\{1 - 0.16[\chi(F) - \chi(Mn)]$$
$$- 0.035[(\chi(F) - \chi(Mn)]^2\},$$

where χ's are electronegativities. Using Pauling's values of electronegativities, $\chi(F) = 4.0$ $\chi(Mn) = 1.4$, the calculated covalency is 0.0637. From Matumura's plot the expected
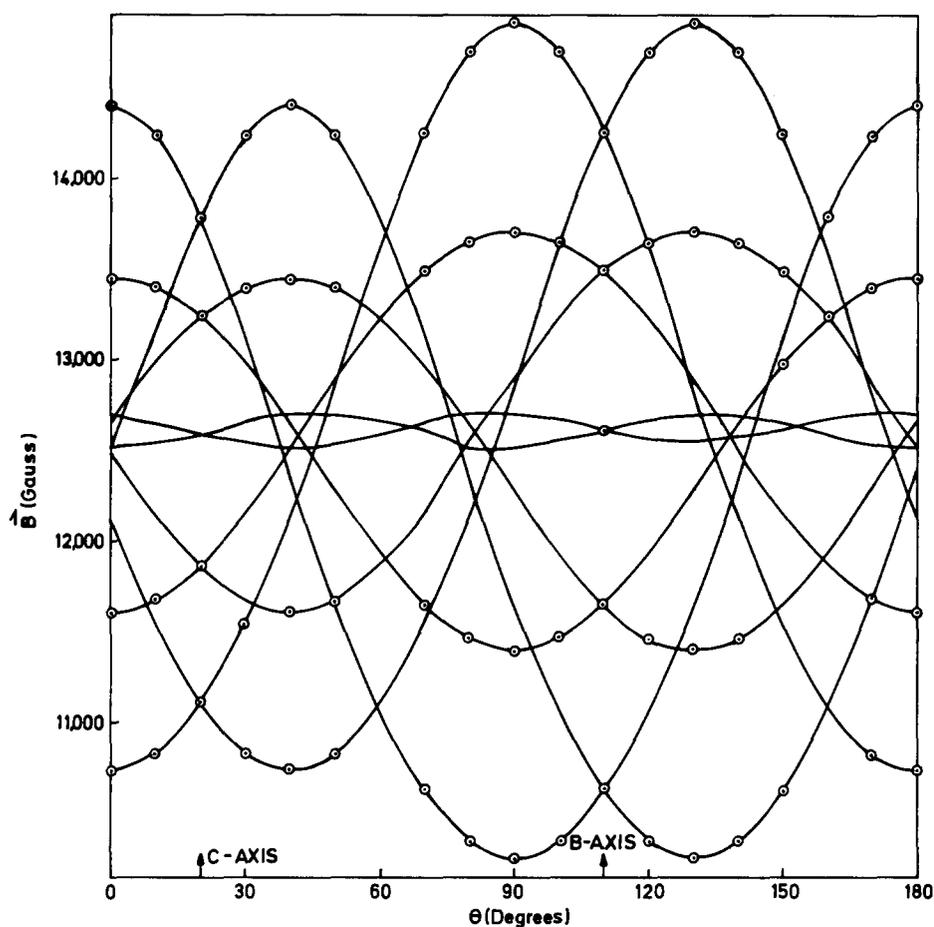
FIG. 5. The angular variation of the fine structure transitions for Mn(II) in $(NH_4)_2SbF_5$ (a) for rotation about a axis, (b) for rotation about c axis. O expt., —calc.

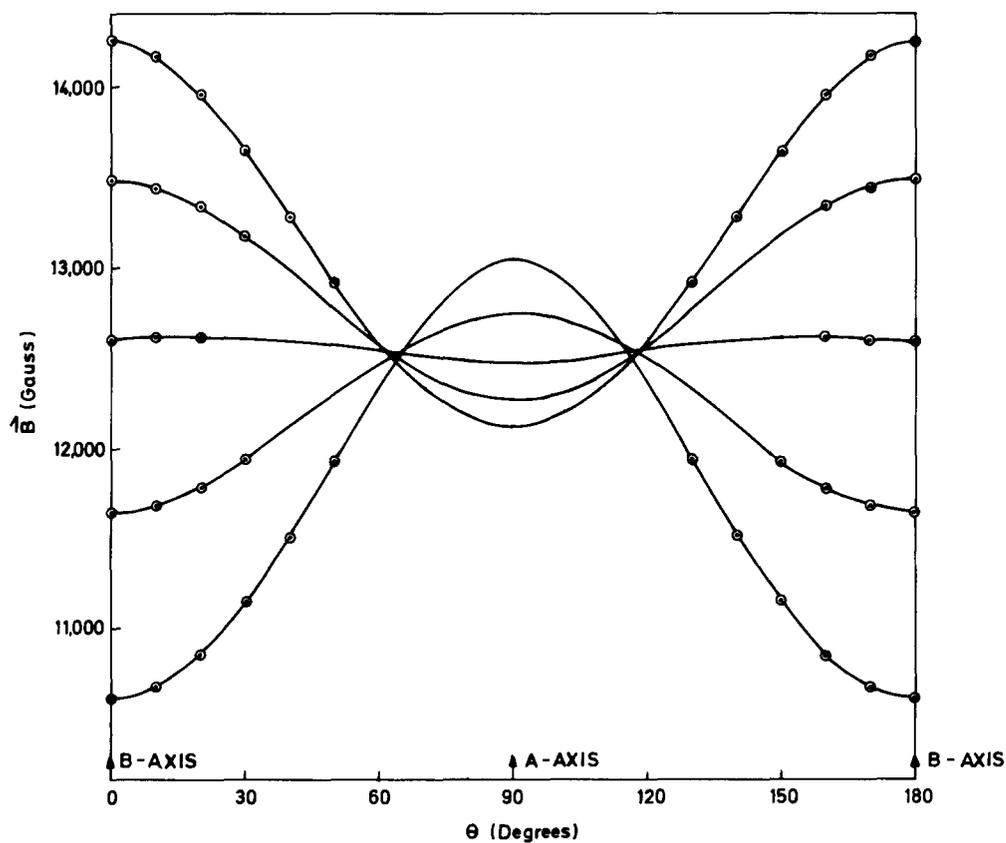TABLE I. Magnetic parameters for Mn(II) in $(NH_4)_2SbF_5$.

	Parameter	Value (cm^{-1})	Direction cosines		
D tensor site 1	D_{xx}	-0.0072	1	0	0
	D_{yy}	-0.0286	0.0	0.3420	0.9396
	D_{zz}	0.0358	0.0	0.9396	-0.3420
D tensor site 2	D_{xx}	-0.0072	1	0	0
	D_{yy}	-0.0286	0.0	-0.3420	0.9396
	D_{zz}	0.0358	0.0	0.9296	0.3420
	^{55}Mn $\quad A_{iso} = 0.0095$ cm^{-1}				
	^{19}F $\quad A_{max} = 0.0018$ cm^{-1}				
	$\quad A_{min} = 0.0015$ cm^{-1}				

hyperfine coupling is 0.0087 cm^{-1}, whereas experimental value is 0.0095 cm^{-1}. It is worth pointing out that the Matumura's empirical relation may not hold for systems in which the Mn–ligand bonds are more than 90% ionic. Nevertheless, similar comparisons[16] do give satisfactorily the ionicity of the d^5 ions such as Fe^{3+}, Cr^+, and Mn^{++}.

As far as the ligand fluorine hyperfine is concerned, it should be pointed out that there is no resolvable hyperfine from apical fluorine and the four equatorial fluorines are equivalent with hyperfine coupling ranging from $a_{max} = 18$ G, $a_{min} = 15$ G. This leads to about 0.2% spin density in the fluorine p orbital and approximately 0.1% in the s orbital. It can be safely concluded that the hyperfine interaction is one of "transferred" type with no direct delocalization via orbital overlap; this is in confirmity with high ionicity of MnF_5 moeity calculated from Matumura's plot. The absence of apical fluorine hyperfine coupling in contrast to large coupling observed in the corresponding Fe(III) analog is rather curious. It is possible that the exact location of

Mn(II) is a fraction of angstrom unit below the F_4 plane. This will account for slight reduction in the hyperfine coupling to basal fluorines in the present case compared to that of Fe(III) analog, and to total absence of apical F coupling.

CONCLUSIONS

The effect of charge compensating interstitial in Mn(II) doped $(NH_4)_2SbF_5$ has been analyzed in terms of the electron spin resonance D tensor. It has been shown that the charge compensating influence leads to distortions in the lattice producing doubling of sites and displaces the Mn(II) cation away from the apical fluorine. This has also been verified by a model MO calculation. The Mn–F bonds have been found to be nearly ionic. The EPR parameters have been confirmed by solving the Hamiltonian using the total diagonalization procedure.
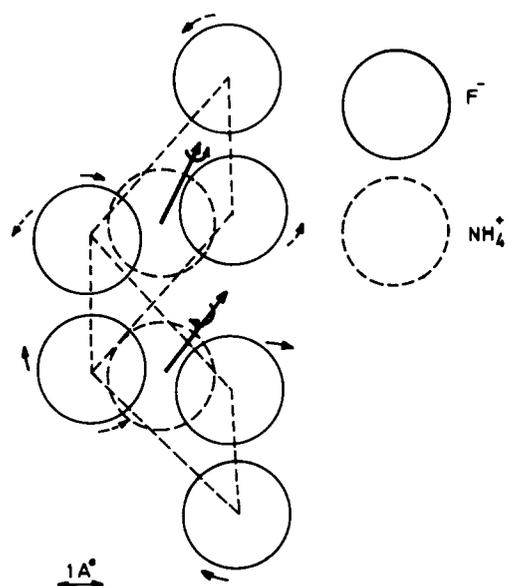
ACKNOWLEDGMENT

FIG. 6. Projection of a part of $(NH_4)_2SbF_5$ lattice about the a axis showing the effect of charge compensating interstial $(NH_4)^+$ ion. The MnF_5^{3-} and the neighbor SbF_5^{2-} units were "twisted" about a axis in order to achieve minimization of energy.

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