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Experimental contribution to the study of S-state ions in ionic single crystals†

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Abstract. Experimental results are reported on S-state ions incorporated into PbFCl-type tetragonal single crystals. The spin Hamiltonian parameters of these ions are determined and correlated with structural and physico-chemical properties of the studied compounds. The experimental b_2^0 spin Hamiltonian parameters vary linearly with the lattice constant a of the host unit cell. Further, the dependence of the spin Hamiltonian parameters on temperature has been investigated and parametrised. The results of a Raman investigation of the hosts are presented.

1. Introduction

Although considerable experimental and theoretical work has been performed on S-state ions incorporated into single crystals, no final understanding of the mechanism(s) of their ground state splitting has been achieved up to now. Within the experimental approach to this problem there has been the tendency in the past to neglect the following two aspects. The first one concerns the choice of the host crystal. Relatively few experimental investigations have been published which cover a set of host crystals sufficiently completely so that valid structural as well as physico-chemical comparisons are possible. The second one lies in the fact that the properties of these clusters (S-state ion + host crystal surroundings) are investigated almost exclusively by magnetic resonance techniques. Other spectroscopic techniques which are complementary are less frequently used. Often they are not applied to the same system as the magnetic resonance experiments. For these reasons we decided to investigate a certain number of paramagnetic systems, varying both the S-state ion and the host crystal within an isomorphous set. We made use of the following spectroscopic techniques: x-ray diffraction, EPR (electron paramagnetic resonance), Raman, optical excitation and luminescence spectroscopy, ENDOR (electron nuclear double resonance).

Our investigation aims at setting up some experimental relations between the ground state splitting (reflected by the usual spin Hamiltonian parameters) and various physico-chemical properties of the host crystals. The present paper represents a partial account of this investigation.

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2. Physico-chemical characteristics of the host crystals

The compounds investigated are alkaline earth halide mixed-crystals of the layer type having the general formula MeFX with Me = Ca, Sr, Ba and X = Cl, Br, I. More specifically we carried out our experiments on the following compounds: CaFCl, SrFCl, BaFCl, BaFBr and BaFI. The former three present only a modification of the alkaline earth cation, while the three latter ones are characterised by the modification of the X halogen. An equimolecular mixture of MeF_2 and MeX_2 powders is prepared and the desired impurity is added at a concentration ranging from 1 to 10‰ (atomic weight). Beforehand the powders had been very carefully dried under vacuum to prevent any hydrolysis. Then the single crystals were grown either by the Bridgman or the Czochralski method, the latter one yielding generally bigger samples (typically of the order 10 × 5 × 1 mm). The crystals were grown in an oxygen-free atmosphere under ultrapure argon gas (0·2 atm). We chose these compounds because they all crystallise in the same structure (space group $P4/nmm$—crystal point group D_{4h}). Further, the position of the ions in the unit cell is well known for all of them (Sauvage 1974, Liebich and Nicollin 1977).

In figure 1 is represented a choice of the unit cell for the MeFX-type lattice. The cell constants c and a together with the crystallographic parameters u and v permit the exact determination of the positions of all the atoms in the cell.

The nearest neighbourhood of the cation Me consists of the set of four fluorines and five X halogen ions. Among these five X halogens only four are equivalent. The fifth one is farther away in CaFCl, BaFBr and BaFI and nearer in the remaining two. The local symmetry of the cationic site corresponds to the C_{4v} point group.

This somewhat schematic way to look at the structure, however, does not really satisfactorily describe the actual interaction scheme within the crystal. In figure 2 is

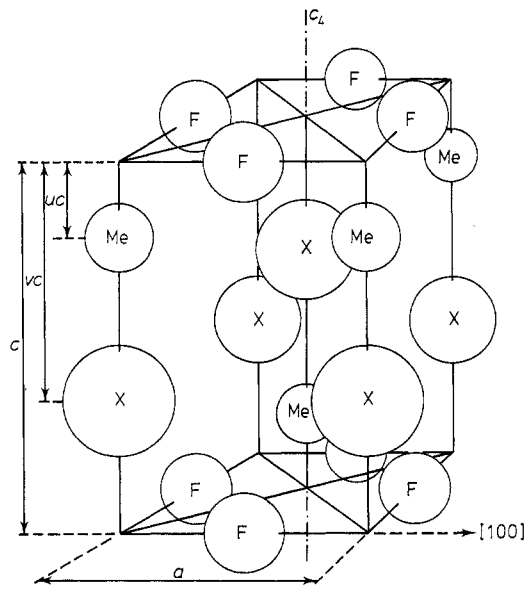

Figure 1. Unit cell for the MeFX-type compound Me—alkaline-earth metal (Ca, Sr, Ba) X—halogen (Cl, Br, I).

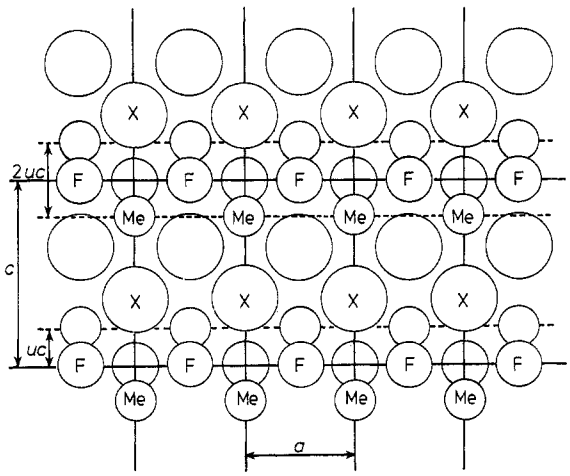

Figure 2. Projection of a portion of an MeFX crystal on an (a, c) plane. The atoms labelled Me, F and X pertain to the same plane (plane of the figure). The blank atoms are also contained in a common plane parallel to the former but displaced by the distance $a/2$.

shown a pictorial representation of a portion of the crystal more appropriate for an adequate discussion of the structural characteristics of these compounds. The crystals can be visualised as being built up from sheets consisting of Me and F atoms with a double layer of X ions between two adjacent sheets.

This concept is supported by the fact that the thickness of a sheet defined by the product $2uc$ is almost constant whatever the nature of the X halogen (Flahaut 1974). It should be noted at this point that the Me–F distances are always very close to the values calculated from the sum of the ionic radii $r_{Me^{2+}} + r_{F^-}$. This is not true for the Me–X distances.

Thus, the following scheme can be proposed (Rulmont 1974) for the distribution of the bonding forces within the crystal:

(i) sheets consisting of the Me and F atoms in which the bonds are strong

(ii) a double layer of X halogens with a comparatively weak bond acting between them.

These assertions are confirmed by several experimental results including for instance the values of the force constants (Marculescu 1973) and the fact that MeFX single crystals cleave very easily along planes perpendicular to the C_4 axis. Probably the double layers of X halogens are separated.

To our knowledge, the temperature of fusion of the compound BaFBr has only recently been reported by Bhat *et al* (1977). They give the value $T = 1060 \pm 10°C$, not in agreement with our results. We found $T = 994 \pm 5°C$. We also determined this quantity for BaFI which was found to be at $T = 893 \pm 5°C$. The two compounds seem to melt in a congruent way.

3. Spin Hamiltonian parameters

3.1. Experimental results

The systems investigated were the S-state ions Mn^{2+}, Fe^{2+}, Eu^{2+} and Gd^{3+} in the host crystals CaFCl, SrFCl, BaFCl, BaFBr and BaFI. For various reasons which will be

discussed below, not all of the systems produced an EPR spectrum. In all the other systems a set of lines was identified which arises from the S-state ion substituting for a cation in the otherwise unperturbed lattice. All of the observed trivalent ions involved one of two types of charge compensation. The centres reported in the following have distant charge compensation. Occasionally we have observed weak spectra of low symmetry which could be traced back to centres having local charge compensation (involving probably an oxygen neighbour). No investigation has been performed on the detailed nature of the charge compensation. The symmetry of each of the centres was determined from the recorded angular dependence of its EPR spectrum. The spectra were parametrised with the appropriate spin Hamiltonian which has the structure corresponding to tetragonal symmetry:

$$\mathcal{H} = g\beta \boldsymbol{B}.\boldsymbol{S} + b_2^0 O_2^0/3 + (b_4^0 O_4^0 + b_4^4 O_4^4)/60 + (b_6^0 O_6^0 + b_6^4 O_6^4)/1260.$$

The hyperfine energy given by $\boldsymbol{S}.\mathbf{A}.\boldsymbol{I}$ has to be added to this expression for Mn^{2+} and Eu^{2+} (both $I = \frac{5}{2}$). A transferred hyperfine interaction term $\sum_\lambda \boldsymbol{S}.\mathbf{T}_\lambda.\boldsymbol{I}_\lambda$ is further needed for Mn^{2+}. The spin Hamiltonian given in this form can be used for all S-state ions (for $3d^5$ ions up to fourth order only as these ions give $^6S_{5/2}$ as the ground state in the $^{2S+1}L_J$ Russell–Saunders terminology). There are in fact several possibilities to define b_2^0 for d^5 ions with $J = \frac{5}{2}$ (Abragam and Bleaney 1969). We choose $b_2^0 = 3B_2^0 = D$ (Hutchings 1964) to obtain results which can be compared directly with those of other authors.

The experimental parameters we obtained for the different systems are summarised in table 1. The final values given here correspond to the smallest deviation between the experimental data and those given by a procedure of minimisation performed with the aid of a computer. The estimated error is of the order of 0·5 (10^{-4} cm^{-1}) on the b_2^0 parameter. The sign of the parameters has been determined at liquid helium temperature.

Table 1. Spin Hamiltonian parameters of the investigated systems. (T: K, b_k^q: 10^{-4} cm^{-1}, A: gauss).

Manganese

Crystal	Temperature	g	b_2^0	b_4^0	b_4^4	^{55}A
SrFCl†	Room	2·0010	591·5	−0·3	4·3	−98·4

Gadolinium

Crystal	Temperature	g	b_2^0	b_4^0	b_6^0	b_4^4	b_6^4
CaFCl	294	1·9913	−48·2	−4·6	−0·2	45·5	−2·3
SrFCl	293	1·9915	30·4	−3·6	−0·2	49·9	−1·7
BaFCl	295	1·9913	84·3	−2·4	−0·3	58·7	−1·2

Europium

Crystal	Temperature	g	b_2^0	b_4^0	b_6^0	b_4^4	b_6^4	^{151}A
CaFCl	293	1·9878	−933·6	9·3	0·4	0·0	0·0	−38·5
SrFCl	292	1·9909	−448·3	9·3	0·4	1·1	3·5	−35·7
BaFCl	300	1·9923	34·1	8·5	0·2	0·0	0·0	−35·1
BaFBr	290	1·9921	245·9	9·0	0·4	28·4	4·0	−34·9
BaFI	291	1·9914	541·8	12·0	0·5	43·1	4·1	−34·1

† Cevey and Lacroix (1970)

Among the possible combinations of the four S-state ions with the host compounds several ones either do not show any spectrum or then they produced ill-resolved ones. Manganese gave only a conventional EPR spectrum in SrFCl. In the other hosts this ion displays interesting motional effects. A study is in progress.

Further, it was also impossible to study the behaviour of trivalent iron in these compounds. The incorporation of iron ultimately results in the formation of F centres similar to those described by Yuste *et al* (1976). Incidentally, this method gives a rather high concentration of F centres. Finally, gadolinium introduced into the hosts BaFBr and BaFI did not produce any EPR spectrum. Optical measurements performed on these systems, however, demonstrated that the Gd ions had entered the crystals. Moreover, its excitation spectrum strongly resembles the one observed in CaFCl, SrFCl and BaFCl. Thus the rare earth ion seems to be in the state Gd^{3+}. The formation of clusters might explain these results. A much less plausible hypothesis suggests a very large and negative zero-field splitting acting on the ground state. Finally, motional effects might be involved although these are less likely to explain the absence of any EPR spectrum because nowhere between 4·2 and 300 K were any resonances observed.

The systems $SrFCl:Mn^{2+}$, $SrFCl:Eu^{2+}$ and $SrFCl:Gd^{3+}$ have already been investigated by EPR (Cevey and Lacroix 1970, de Siebenthal *et al* 1974, Zevenhuijzen *et al* 1976). Our results are in good agreement with these results except for the experimental value b_2^0 ($= D$) quoted by Zevenhuijzen. This parameter is significantly different (about 40 G) from the one reported by Cevey and Lacroix which coincides with our results.

3.2. *Systematics*

The dependence of the b_2^0 parameter on the host matrix is pronounced for Eu^{2+} and is rather small for Gd^{3+}. The excess positive charge of this latter ion relative to the charge of the host cation which it substitutes for probably attracts the anion neighbours. A local cluster has its structure determined essentially by this interaction and only slightly by the lattice dimension of the particular host. We have plotted in figure 3 the experimental

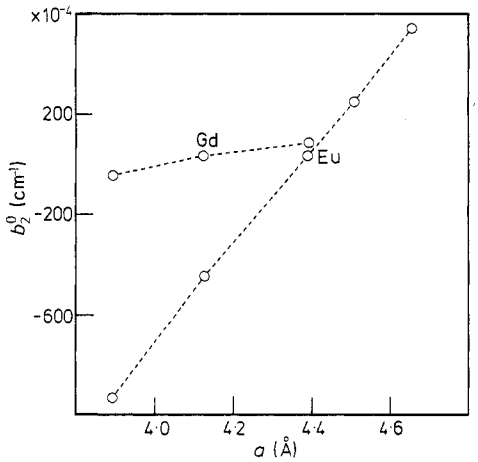

Figure 3. Spin Hamiltonian parameter b_2^0 for Eu^{2+} and Gd^{3+} versus the lattice constant a of the compounds reported in this paper.

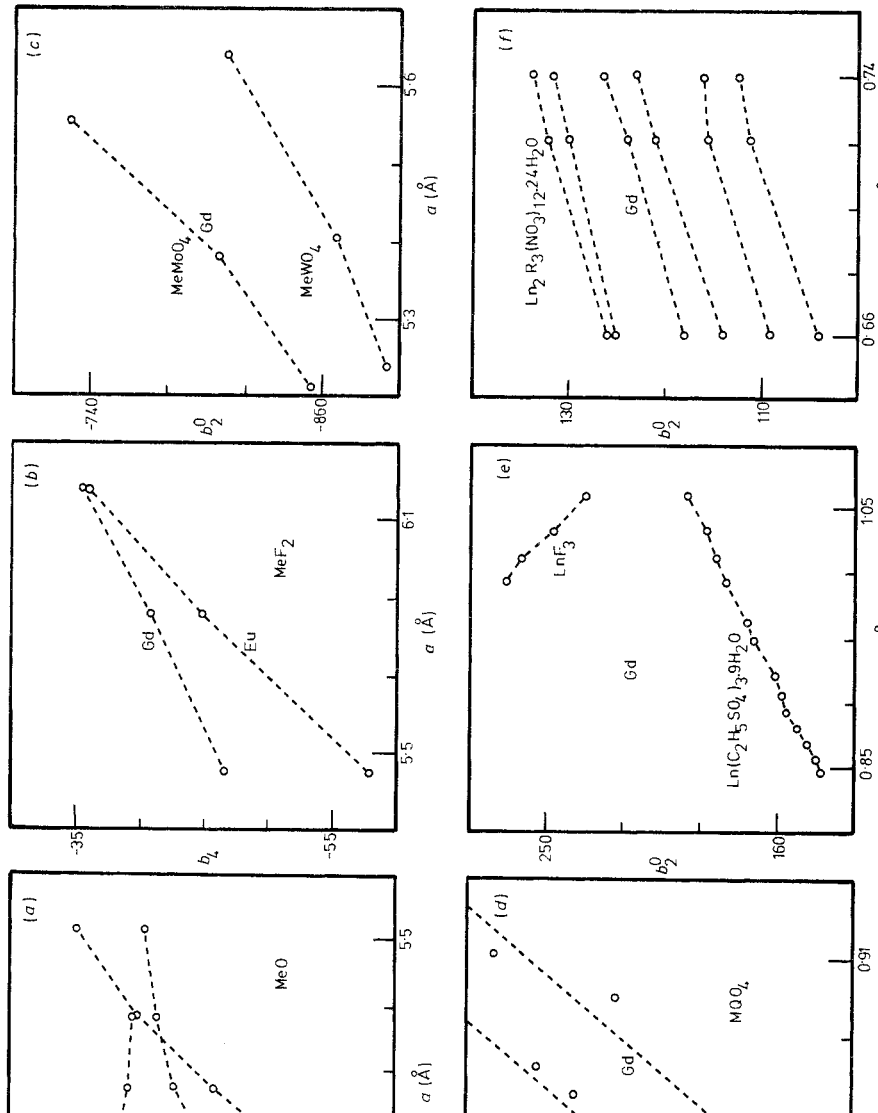

Figure 4. Spin Hamiltonian parameters compiled from the literature. They have been plotted versus 'geometrical environment'. (Units: 10^{-4} cm^{-1}, b_4: cubic symmetry, b_2^0: lower symmetry.) (*a*) Overmeyer and Gambino (1964), Miyata and Argyle (1967), Abraham *et al* (1971), Rubio *et al* (1977), O'Connor *et al* (1977): (*b*) Miyata and Argyle (1967), Title (1963): (*c*) Vinokurov and Stepanov (1967): (*d*) Urban (1971): (*e*) Viswanathan and Wong (1968), Buckmaster *et al* (1972), Gerkin and Thorsell (1972), Sharma V K (1971): (*f*) Misumi *et al* (1974), Misumi *et al* (1975).

parameter b_2^0 versus the lattice constant a for Gd^{3+} and Eu^{2+}. In addition to the feature pointed out above the figure shows that the experimental points fit very closely to a straight line. These results seen to confirm the hypothesis of Munoz *et al* (1975) who postulate a relation $b_2^0 \propto r$, r being the distance from the rare earth to the neighbour anion. Note that the electrostatic model implies a relation of the kind $\log b_2^0 \propto \log r$.

Several investigations regarding the dependence of the spin Hamiltonian constants on physical and crystallographic parameters have been published. In figure 4 we have summarised some of these results which are scattered through the literature. We do not wish to discuss them in detail (the reader should refer to the references given under the figure). The reason why they are given is to show that the experimental linear relation between the pertinent spin Hamiltonian constant b_k^q and an appropriate lattice parameter (valid for the presently reported systems) is in fact observed for the S-state ions in many sets of isomorphous host crystals as displayed in figure 4. The host compounds include the following widely differing structures: alkaline earth oxides MeO, alkaline-earth fluorides MeF_2, scheelite $MeMoO_4$–$MeWO_4$ and zircone-type MQO_4 crystals, lanthanide ethylsulphates $Ln(C_2H_5SO_4)_3 \cdot 9H_2O$, lanthanide fluorides LnF_3 and lanthanide double-nitrates $Ln_2R_3(NO_3)_{12} \cdot 24H_2O$. Other features of our results are as follows. For europium, the value of the b_2^0 parameter increases with the degree of covalency of the bonds between the paramagnetic ion and the ligands in the various compounds. This assertion assumes that covalency is reflected by the decreasing absolute value of the hyperfine structure constant A given in the last column of table 1 (Simanek and Müller 1970, Kojima *et al* 1976). Similar trends are observed in alkaline earth oxides for Eu^{2+} (Overmeyer and Gambino 1964, Abraham *et al* 1971) and Mn^{2+} (Abragam and Bleaney 1969, Rubio *et al* 1977), in alkaline earth fluorides for Eu^{2+} (Title 1963) or in ZnZ compounds (Z = O, S, Se, Te) for Mn^{2+} (Abragam and Bleaney 1969). The spectroscopic g factor of europium also shows a typical trend. It takes a maximum value for the compound BaFCl. This behaviour seems to be related to the position of the excited electronic levels (especially the $4f^6 5d$ levels) as shown by the study of the optical spectra (Nicollin 1977).

From the study of the transferred hyperfine interaction of the system $SrFCl:Mn^{2+}$ a value of 64° is obtained (Cevey and Lacroix 1970). This value can be interpreted as corresponding to the angle between the bond axis S-state ion to the fluorine ligand and the C_4 axis. The x-ray diffraction measurements on the unperturbed crystal give 55·8° for the angle between the internuclear direction Sr–F and the C_4 axis. Thus, if the fluorine ligands maintain the same position in the paramagnetic complex with respect to the undoped crystal, a higher value of the angle can be visualised as a displacement of the impurity towards the plane containing the fluorine ligands. Preliminary ENDOR measurements do show a similar trend for the systems $SrFCl:Gd^{3+}$ and $BaFCl:Gd^{3+}$. These results seem to confirm the greater interaction within the sheet containing the metal (alkaline earth or S-state ion) and the fluorine ions as discussed in the preceding section. The linear dependence between the b_2^0 parameters and the lattice constant a (which determines also the fluorine–fluorine distances) suggests a similar conclusion.

We have applied the Newman model (Nicollin and Bill 1976) to the systems investigated. For details concerning this model the reader should for instance consult the article written by Newman and Urban (1975). The calculations were performed for all the systems and were based on the undisplaced position of the ions in the host lattice. The results are not given because many of them are not really satisfactory. A necessary prerequisite for a successful test of this model is the detailed knowledge of the local geometry of the S-state ion cluster. ENDOR experiments are in progress which will give a more realistic local structure.

3.3. Influence of the temperature on the ground state splitting

The temperature dependence of the spin Hamiltonian parameters has been investigated for the systems under study. The essential point is that the results obtained for all the systems have a dependence on the temperature T which is well exemplified by figure 5. Among the physical models proposed for the interpretation of the experimental results the following ones have found widespread applications: that of Pfister *et al* (1969), that of Shrivastava (1969) and more recently that of Bates and Szymczak (1976). Two different relations can essentially be deduced from these models but we have found that they fit our results equally well within the precision of the experiments when certain relations are fulfilled between the two sets (one for each model) of adjustable constants (Bill 1978). For this reason the experimental results have been parametrised with the aid of the following expression

$$b_k^q(T) = b_k^q(0) + B_k^q \coth C_k^q/T$$

where B_k^q and C_k^q are adjustable parameters. The constant C_k^q is equal to $h\nu_k^q/2k$ (k = Boltzmann constant, h = Planck constant) where ν_k^q is the frequency of the local mode in the model of Pfister *et al* (1969).

The temperature dependence of the b_2^0 parameter was measured. The variation of the other spin Hamiltonian parameters is much less pronounced and in all cases small in absolute value and of the order of the errors of the experiments. Figure 5 shows the fitted function together with the experimental points for the system SrFCl: Eu^{2+}. The parameters $b_2^0(0)$, B_2^0, C_2^0 and $\bar{\nu}_2^0$ obtained by fitting this function to all our results are collected in the table 2. At high temperature the variation of $b_2^0(T)$ is given approximately by the ratio B_2^0/C_2^0. For all our systems except SrFCl: Mn^{2+} this ratio is positive. Thus, b_2^0 increases

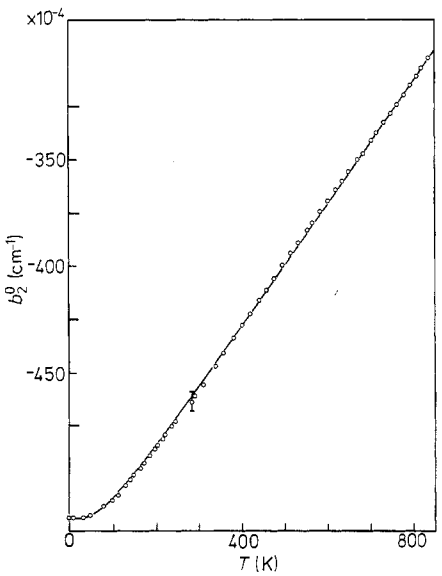

Figure 5. Variation of the experimental parameter b_2^0 with temperature for the system SrFCl: Eu^{2+}. The circles represent the experimental values obtained from the EPR spectrum, the full line corresponds to an analytical hyperbolic cotangent.

Table 2. Compilation of the parameters describing the variation of b_2^0 with temperature. The values given in the table are those which are involved in the expression $b_2^0(T) = b_2^0(0) + B_2^0 \coth C_2^0/T$. ($b_2^0(0)$: 10^{-4} cm^{-1}, B_2^0: 10^{-4} cm^{-1}, C_2^0: K, $\bar{\nu}_2^0$: cm^{-1}).

Manganese

Compound	$b_2^0(0)$	B_2^0	C_2^0	$\bar{\nu}_2^0$	B_2^0/C_2^0
SrFCl	688·3	−15·7	44·0	61	−0·357

Gadolinium

Compound	$b_2^0(0)$	B_2^0	C_2^0	$\bar{\nu}_2^0$	B_2^0/C_2^0
CaFCl	−74·2	4·6	60·0	83	0·077
SrFCl	4·0	6·5	75·0	104	0·087
BaFCl	50·2	5·9	56·0	78	0·105

Europium

Compound	$b_2^0(0)$	B_2^0	C_2^0	$\bar{\nu}_2^0$	B_2^0/C_2^0
CaFCl	−1024·5	23·2	85·0	118	0·273
SrFCl	−531·1	25·1	93·5	130	0·268
BaFCl	−15·6	9·8	62·0	86	0·158
BaFBr	206·7	4·4	33·0	46	0·133
BaFI	525·0	1·2	21·0	29	0·057

with temperature. This is in line with the fact that most of the spin Hamiltonian parameters b_4 (cubic) and b_2^0 (symmetry less than cubic) of Gd^{3+} are negative and that their absolute value decreases with an increase of temperature (Buckmaster and Shing 1972, Abraham and Boatner 1969, Vinokurov and Stepanov 1967). In several zircon and double nitrate-type compounds a parallelism is observed between the variation of b_2^0 and the degree of anisotropic expansion of the unit cell with temperature (Misumi *et al* 1975, Kahle *et al* 1970).

It is interesting to see that the parameters B_2^0 and C_2^0 (Eu^{2+} and Gd^{3+}) vary in the same sense from one system to another. They have a maximum both for Eu^{2+} and Gd^{3+} in the host compound SrFCl. Notice that this is the only compound where the Mn^{2+} ion shows an EPR spectrum which is entirely resolved.

The effective frequency $\bar{\nu}_2^0$ and thus θ obtained for the systems considered show the tendency to decrease from CaFCl to BaFI.

4. Raman properties of the compounds

It seemed to us important to obtain some information regarding the lattice dynamical properties of the host crystals. The fact that the coth function was used to parametrise the paramagnetic resonance results as presented in the foregoing section does not imply the presence of strongly localised Einstein-type vibrations. Instead, the whole lattice phonon spectrum contributes. A detailed search for Raman active pseudo-localised modes has indeed largely confirmed this assertion.

A Raman investigation of the hosts SrFCl, BaFCl and BaFBr has already been performed (Scott 1968). The normal modes at the Brillouin zone centre are:

$$2A_{1g}(R) + B_{1g}(R) + 3E_g(R) + 2A_{2u}(IR) + 2E_u(IR).$$

The activity of each vibration is specified by R (Raman active) and IR (infrared active). Six vibrations are expected to be observed in Raman spectroscopy.

Figure 6 shows a typical Raman spectrum recorded at room temperature and the parameters deduced from the experiments are collected in table 3. The estimated absolute error on the position of the transitions is 2 cm^{-1}. Polarisation measurements have permitted to assign the symmetry of the vibrations.

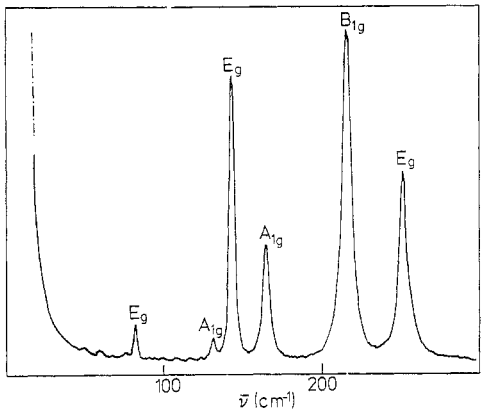

Figure 6. Raman spectrum of the BaFCl compound. The six vibrations predicted by group theory are clearly seen on the spectrum: $\bar{\nu}$ represents the relative displacement of the Stokes transitions with respect to the laser excitation at zero wavenumber.

The following facts need some supplementary considerations. The frequency of the modes B_{1g} and E_g show a comparatively small dependence on the host lattice. From symmetry arguments it follows that the B_{1g} mode only involves F^- ion displacements. The very small variation of $\bar{\nu}(B_{1g})$ as a function of the three hosts BaFCl, BaFBr and BaFI strongly supports the crystal structure discussed in §2. The Ba–F bond seems to be very slightly affected by the X halogen ion. The rather small change of the frequency of the high-frequency E_g mode as a function of the host lattice suggests that it involves mainly F^- ion displacements too. A similar behaviour is observed for the high-frequency odd parity modes A_{2u} and E_u (Bhat *et al* 1977, Rast *et al* 1971, Marculescu 1973). Similar

Table 3. Wave numbers and symmetries of the Raman vibrational modes of the MeFX compounds (cm^{-1}).

Compound	E_g	A_{1g}	E_g	A_{1g}	B_{1g}	E_g
CaFCl	156	192	209	265	252	336
SrFCl	107†	155†	164	194	241	296
BaFCl	82	132	143	165	216	251
BaFBr	76	103	109	123	211	238
BaFI	67	78	111	102	203	219

† Scott (1968).

features of these modes are observed in the isostructural compounds PbFX and BiOX (Rulmont 1974, Bonnaire 1968).

Qualitatively, the vibrations should depend on the cell dimension a. This is indeed the case, the variation of the frequencies B_{1g} and E_g between the compounds CaFCl and BaFCl being greater than the one between BaFCl and BaFI. For the other four low-frequency modes, in which both the alkaline-earth metal Me and the halogen X have an amplitude of vibration different from zero, one would expect a general decrease of the frequency with increasing mass of either the metal or the halogen. The values given in table 3 do indeed show such a trend.

The point group of the host crystal is D_{4h}. One effect of the impurity ions is to reduce this group locally to C_{4v} in addition to the local destruction of the pure translation group. Raman experiments are in progress in strongly doped crystals and in crystals of the type $Me^{I}_{1-x}Me^{II}_{x}FX$($Me^{I}$, Me^{II}: Ca, Sr, Ba) to investigate some of the consequences of this fact.

5. Conclusions

In this paper we have reported the experimental results of several S-state ions incorporated into an isomorphous set of host crystals. The investigated systems show a remarkably simple relation between the dominant spin Hamiltonian constant and an appropriate lattice parameter. In addition, our Raman measurements compared to the temperature dependence of the S-state ion crystal-field splitting indicate that probably the paramagnetic complexes do not involve strongly localised lattice vibrations.

A further, though indirect, result is the fact that the Newman model gives incoherent results for these systems when the geometry of the undistorted crystal is assumed. This result is not too surprising in the light of the discussion regarding the structural properties of the systems given in the paper.

It seems to us that experimental work can still contribute to the problem of the ground state splitting of the S-state ions but as also quoted by Munoz *et al* (1975) only by means of systematic investigations.

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