

Paramagnetic Resonance of S-State Ions in Strontium Chloride†

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Paramagnetic resonance spectra have been observed of Mn^{2+} , Gd^{3+} , and Eu^{2+} in single crystals of strontium chloride grown from the melt. The Mn^{2+} shows a very small cubic-field splitting $a < 1 \times 10^{-4} \text{ cm}^{-1}$ and a hyperfine structure constant of $A = 81.2 \times 10^{-4} \text{ cm}^{-1}$, indicating some covalent bonding. The Gd^{3+} and Eu^{2+} have cubic symmetry with splitting parameters, for Gd^{3+} : $c = \pm(39.6 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$, $d = \mp(0.2 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$, $g = 1.9906 \pm 0.001$; for Eu^{2+} : $c = (52 \pm 5) \times 10^{-4} \text{ cm}^{-1}$, $A^{151} = (34.5 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$, $A^{153} = (15.5 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$, $g = 1.995 \pm 0.001$.

The smaller cubic field splittings in SrCl_2 compared with CaF_2 seem to favor a mechanism responsible for the cubic-field splitting which is linear in the crystal potential terms.

INTRODUCTION

THE properties of some paramagnetic ions of the iron group and rare earth group substituted as impurities in single crystals of calcium fluoride have recently been investigated.¹⁻⁵

The properties of these ions in the fluorite symmetry are of particular interest, since, if the cubic symmetry is preserved, the order of the Stark levels is inverted compared with octahedral symmetry.

For a number of reasons it seemed advisable to study these ions in another matrix of the same symmetry as calcium fluoride. First of all, the spectrum of the iron group in calcium fluoride is of considerable complexity because of the many lines caused by the hyperfine interaction with the adjacent fluorine nuclei. Very often these lines are not resolved and the lines are broadened considerably. Second, it has been noticed that in CaF_2 some of the trivalent ions can be substituted for the calcium without disturbing the cubic-field symmetry.^{2,3} Other ions, however, give rise to paramagnetic resonance spectra which can only be interpreted with a spin Hamiltonian of axial symmetry. This has been interpreted to arise from an extra F^- ion occupying the nearest vacant interstitial site.^{4,5} For one particular ion, gadolinium, it became apparent that in some calcium fluoride crystals the cubic symmetry was preserved whereas in others a large tetragonal distortion is detected. Since the radius of the strontium ion is larger than the calcium ion, it was felt that the trivalent ions of the rare earth group could be substituted with less difficulty.

For these reasons we have embarked on a systematic intensive study of the magnetic and optical properties of transition elements in strontium chloride. This paper

reports an investigation on ions which can easily be studied at room temperature, i.e., S-state ions. These ions comprise Mn^{2+} , Fe^{3+} , Gd^{3+} , and Eu^{2+} . All these ions, with the exception of Fe^{3+} , could be substituted with relative ease for strontium. The paramagnetic resonance spectrum of Fe^{3+} could not be detected, although chemical analysis proved it to be present in the crystal. Presumably the trivalent ion is not located substitutionally and may aggregate along dislocations. It is also possible that part of the trivalent iron may have been reduced to divalent iron during the crystal growth. The spectrum of Fe^{2+} would not have been detected at room temperature because of its very short relaxation time.

EXPERIMENTAL DETAILS

Strontium chloride is the only chloride to crystallize in fluorite symmetry. It belongs to the O_h^5 space group. The unit cell is relatively large.

A number of attempts were made to grow single crystals of strontium chloride before good transparent crystals were obtained. In the final arrangement the strontium chloride powder was dehydrated by baking it at a few hundred degrees under vacuum. This is particularly important since any moisture present in the original powder gives rise to white or opaque crystals which upon being exposed to air disintegrate slowly into a white powder. If the crystal is grown with care it remains stable for several weeks without any special precautions. Strontium chloride crystals seem, however, to be particularly hygroscopic to organic vapors.

The crystals were grown in a closed quartz tube under a vacuum of about 10^{-2} – 10^{-3} mm Hg. It was found that the crystals grew better in quartz tubes than in Vycor tubes. In Vycor tubing the powder tends to react with the glass and on cooling the single crystal breaks into a number of small crystals.

The crystals were grown at about 900°C . The quartz tube was lowered through a sharp gradient of about 200°C . The rate of lowering was 1–2 cm per hour. The crystals were annealed for several hours at a few hundred degrees C.

The paramagnetic resonance spectra were observed in a conventional X-band or K-band reflection spec-

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¹ W. Low, Phys. Rev. **105**, 793 (1957).

² W. Low, Phys. Rev. **109**, 265 (1958).

³ R. Lacroix, Helv. Phys. Acta **30**, 374 (1957); C. Ryter, Helv. Phys. Acta **30**, 353 (1957).

⁴ Baker, Bleaney, and Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

⁵ Bleaney, Llewellyn, and Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956).

trometer. The crystals were cleaved along the (111) planes, covered with beeswax to prevent the absorption of water vapor, and placed with appropriate wedges into the cavities. The crystals could be rotated about a horizontal axis and the magnet about a vertical axis. In this way the spectrum could be investigated in nearly all important crystallographic planes.

EXPERIMENTAL RESULTS AND DISCUSSION

(a) Manganese, $\text{Mn}^{2+}(3d^5, {}^6S_5)$

The spectrum consisted essentially of six hyperfine lines. It could be interpreted with the usual cubic spin Hamiltonian

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{S}\cdot\mathbf{I} + \frac{1}{6}a[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)], \quad (1)$$

with S and $I = \frac{5}{2}$, $g = 2.0017 \pm 0.0008$, $A = (81.2 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$, and $3a < 1 \times 10^{-4} \text{ cm}^{-1}$.

The magnitude of the cubic-field splitting could be inferred from the line width and partial resolution of the fine structure of the $m = \pm\frac{5}{2}$ and $m = \pm\frac{3}{2}$ lines. The second order hyperfine structure of magnitude $(A^2/2g\beta H)[I(I+1) - m^2 + m(2M-1)]$ causes a splitting of a few gauss for $m = \pm\frac{5}{2}$ and $m = \pm\frac{3}{2}$. The splitting is small for $m = \pm\frac{1}{2}$ since the g factor in manganese is isotropic. This quantity is independent of orientation of the crystal axis with respect to the magnetic field. However the term of the cubic-field splitting varies in magnitude with orientation.

It was found that if the magnetic field pointed along the [100] axis the highest-field line had a square shape of half-width about 16 ± 2 gauss at 3 cm. Using a field modulation of very small depth, this line was resolved into its fine structure components. The intensity distribution, as well as the resolution, varied with orientation. The third and the fourth line were always fairly narrow, of width approximately 6 gauss. The spectrum was also investigated at 1.25 cm. At this frequency the magnitude of the second-order hyperfine structure is considerably smaller. The fine structure could not be resolved, although the line width was less. The angular variation had only a very small effect on the intensity distribution and line shape of the hyperfine lines. This is to be expected if the cubic-field splitting is very small and the fine structure is nearly collapsed. At 3 cm, where the fine structure is partially resolved because of the isotropic second-order hyperfine structure, it is easier to detect the influence of even a small cubic-field splitting. A detailed analysis of the shape of the lines enables us to set an upper limit to the magnitude of the cubic-field splitting $3a$ to be less than $3 \times 10^{-4} \text{ cm}^{-1}$.

The value of a is probably the smallest found so far in any crystal. It is smaller than in CaF_2 .⁴ As will be discussed below, this is to be expected since the crystal field is considerably weaker in SrCl_2 .

The magnitude of A is considerably smaller than in

CaF_2 [$A \sim (97.8 \pm 1) \times 10^{-4} \text{ cm}^{-1}$]^{2,4}. This is probably indicative of covalent bonding.

We should like to point out that these results are at variance with those reported by Dobrowolski *et al.*⁶ These authors find $A = 93.6$ gauss for powdered SrCl_2 at 20°K. To check our results we ground one crystal to powder and prepared, as well, as sintered SrCl_2 powder containing manganese. The results for the powdered specimen were in agreement with those found on the single crystals. In view of this it may be worth while to check the ratio of the moments of $\text{Mn}^{53}/\text{Mn}^{55}$ which these authors have measured on the powdered samples.

(b) Gadolinium, $\text{Gd}^{3+}(4f^7, {}^8S_{7/2})$

Crystals were grown from a mixture containing 0.5% of gadolinium by weight. The paramagnetic resonance spectra indicated less than this amount to be present in the parts of the crystal cleaved off for this investigation.

The spectrum observed showed one ion in the unit cell. It can be described by a cubic spin Hamiltonian, in the notation of Baker *et al.*⁴

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) + A\mathbf{S}\cdot\mathbf{I}, \quad (2)$$

where $240B_4 = c$ and $4 \times 1260B_6 = d$ in the author's notation.² The energy levels and transitions have been given by the author² and by Lacroix.³ The results for the splitting parameters and g factor are listed in Table I. The absolute signs of c and d have not been determined. The sign of d has been found to be opposite of c .

Table I lists the initial splittings of various crystals of fluorite symmetry containing gadolinium.

Wanatabe⁷ has considered the mechanisms responsible for the ground-state splittings of Mn^{2+} and Fe^{3+} in cubic crystalline fields. His reasoning as extended to gadolinium is essentially as follows. Two ions are said to be complementary when the patterns of their Stark splittings are inverted. This occurs for f^m and f^{14-m} . Now f^7 is complementary to itself, and, therefore, would show two patterns, one the inverse of the other. But since a given multiplet shows only one pattern, the f^7 configuration cannot be split by the action of a linear crystal field. It can be split by higher-order perturba-

TABLE I. Cubic field splittings of Gd^{3+} in various crystals of the fluorite symmetry.

Crystal	g -factor	c in 10^{-4} cm^{-1}	d in 10^{-4} cm^{-1}	Reference
SrCl_2	1.9906 ± 0.001	$\pm 39.6 \pm 0.1$	$\mp 0.2 \pm 0.1$	This paper
CaF_2	1.991 ± 0.002	$+185 \pm 5$	-4 ± 2	Low ^a
CaF_2	1.9918 ± 0.001	± 183	∓ 0.3	Ryter ^b
ThO_2	1.9913 ± 0.0005	$\pm 242 \pm 0.8$	$\pm 1.8 \pm 0.8$	Low and Shaltiel ^c

^a See reference 2.

^b See reference 3.

^c See reference 8.

⁶ Dobrowolski, Jones, and Jeffries, *Phys. Rev.* **104**, 1378 (1956).

⁷ H. Wanatabe, *Progr. Theoret. Phys. (Kyoto)* **18**, 405 (1957).

tions involving off-diagonal elements in the square or higher-order cubic potentials.

According to Wanatabe's analysis, the cubic field splitting c would be of the form

$$c = (Dq)^2[a - b(Dq)^2],$$

where Dq represents the usual measure of the cubic field strength, and a and b are constants depending on the detailed nature of the excited states. The quadratic term Dq arises in the main from processes quadratic in the potential and quartic or of higher order in the spin-orbit coupling (or quadratic in Dq and of higher order in spin-spin interaction and spin-orbit interaction). The quartic term in Dq arises from processes quartic in the potential and quadratic in the spin-spin interaction. Since the potential (i.e., Dq) is presumably small for most rare earth ions and the spin-orbit interaction fairly large, the splitting ought to be primarily proportional to the square of the potential or inversely to the tenth power of the interionic distance.

The ratio of the Sr—Cl and Ca—F distance is about 1.28–1.29. Assuming that the trivalent gadolinium ion does not change this ratio appreciably, one can calculate the ratio of the cubic splittings. This gives 11.8 times larger splitting for CaF₂ than in SrCl₂ compared with the experimental ratio of 4.7. The comparison with the data on ThO₂ is more difficult since here the trivalent gadolinium is substituted for the tetravalent thorium.⁸ Assuming that the interionic distances are not changed, one calculates the theoretical ratio of the cubic-field splitting to be about 36 times that of SrCl₂. (This large ratio is caused by the fact that the charge on the oxygen is twice that of the chlorine.) The experimental ratio is about 5.5.

One is, therefore, led to suspect that the mechanism responsible for the splitting is linear in the potential. In this case the agreement is fair. Another possibility is to assume that the Gd—Cl or Gd—F distances differ considerably from the Sr—Cl or Ca—F distances. The ratio of these distance would have to be reduced to 1.08 instead of 1.29 to bring about agreement with the experimental results. There is, however, some additional evidence favoring the first alternative. The ratio of the cubic-field splitting of Eu²⁺ in CaF₂ and SrCl₂ is about 4.5 and therefore very similar to that of gadolinium. It is exceedingly unlikely that the divalent europium would change the interionic distances so drastically and in a similar manner to trivalent gadolinium. Secondly, the temperature dependence of the cubic-field splitting in the lattice of ThO₂ and CaF₂ show that c is changed by only a few percent between room and liquid helium temperatures. If the splitting mechanism were depen-

dent on the square of the potential, a much larger change would have been expected. These data, therefore, favor a mechanism linearly dependent on the potential. (It would be worth while to investigate the spectrum of Gd³⁺ and Eu³⁺ in CaO. Extrapolation from our data indicate that a splitting of about 0.2 cm⁻¹ is expected.)*

Mechanisms linear in the potential can indeed be constructed if one does not limit oneself to the 4f⁷ configurations.⁹ These processes involving higher configurations of the type 4f⁶ 6p or 4f⁶ 6f involve the spin-orbit interaction to the fourth order or the spin-spin interaction in the second order. One would, however, expect that the contribution of these mechanisms to the cubic splitting would be somewhat smaller than those restricted to the 4f⁷ configuration, since the excited energy levels are far removed from the ground state.

Our results give no indication how and where the charge compensation is achieved. The full width at half power of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition is about 2 gauss. Since the spectrum can be fitted with a cubic spin Hamiltonian and since the line width is very narrow, this seems to show that there are no interstitial ions in the neighborhood. In view of the contrary results found by Baker *et al.*⁴ on CaF₂, it is planned to investigate whether the spectrum changes on heat treatment, such as prolonged annealing and quenching.

(c) Europium, Eu²⁺(5f⁷, ⁸S_{7/2})

The spectrum of europium has been previously reported by the author¹⁰ and has also been observed by Hayes.¹¹

The spectrum is similar to that of gadolinium except that the hyperfine structure of isotopes 151 and 153 with spin $\frac{5}{2}$ complicates the spectrum. The total number of lines is 84 consisting of 7 groups which are in part superimposed one on top of the other. Analysis of the spectrum yields the following parameters: $c = (52 \pm 5) \times 10^{-4}$ cm⁻¹, $A^{151} = (34.5 \pm 0.3) \times 10^{-4}$ cm⁻¹, $A^{153} = (15.5 \pm 0.3) \times 10^{-4}$ cm⁻¹, $g = 1.995 \pm 0.001$. This is in fair agreement with the results of Hayes.

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* Note added in proof.—There is some evidence that the cubic field splitting for iron group elements is a quadratic function of the cubic field strength. The evidence presented here is only for some of the rare earth ions. It is possible that in view of the large spin-orbit coupling and deviations from Russell-Saunders coupling for the rare earth ions a different mechanism is operative in the rare earth group.

⁹ J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **19**, 961 (1934).

¹⁰ W. Low, *Phys. Rev.* **101**, 1827 (1956).

¹¹ W. Hayes, quoted in reference 4, Table I.

⁸ W. Low and D. Shaltiel, *J. Phys. Chem. Solids* **6**, 315 (1958).