MINERALOGICAL MAGAZINE, JUNE 1974, VOL. 39, PP. 705–8.

An E.S.R. study of natural fluorite containing manganese impurities

A. D. BAILEY,[1] R. P. HUNT,[2] AND K. N. R. TAYLOR[3]

SUMMARY. The electron spin resonance spectrum of a sample of natural, orange-coloured fluorite from Broken Hill, Australia, has been observed and shown to arise from the presence of manganese ions. From an analysis of the structure of this spectrum it has been possible to estimate the various contributions to the ionic energy level splitting and to show that these are in good agreement with comparable results for synthetic material. It is evident that the manganese ions have entered the lattice substitutionally at Ca^{2+} sites and the nature of this site is discussed.

NATURAL calcium fluoride has long been the subject of investigations using physical, chemical, and mineralogical techniques. These have primarily been concerned with an attempt to understand the coloration of 'Blue John' and similar coloured and colourless fluorites. Until recently the physical techniques have been largely associated with the optical and luminescence properties of these materials (see Przibram (1956) and Schulman and Compton (1963) for references). In the past few years, however, several groups have used electron spin resonance (e.s.r.) observations in an attempt to throw some light on to this, now classical, problem. These measurements have shown a large variety of different spectra (Mackenzie and Green, 1971; Hunt *et al.*, 1973), which appear capable of some degree of correlation with the location of the fluorite deposit, although in general the details of the spectra are not understood. Mackenzie and Green, however, observed a low-intensity, six-line spectrum in one of their samples of Derbyshire Blue John, which they attributed to the presence of manganese impurities. During a recent investigation of fluorites from several deposits, we have carried out electron spin resonance measurements on an orange fluorite (Spec. No. 235, Durham Department of Geological Sciences) from Broken Hill, Australia, which also contained manganese impurities, the results of which will be described in the present paper.

The sample consisted of large transparent crystals averaging about 1 cm^3, from which we cut a 2-mm cube for the e.s.r. measurements. The manganese concentration of the sample was found to be 810 p.p.m. using standard X-ray fluorescence methods. The electron spin resonance system used was a conventional X-band superheterodyne reflection spectrometer using field modulation and having a sensitivity of approximately 10^{14} spins oe.

---

[1] Now at University of Bath, England.

[2] Now at CEGB Nuclear Research Laboratory, Berkeley, England.

[3] Now at Physics Dept. University of N.S.W. Sydney, Australia.

A typical low-resolution spectrum obtained from this specimen, which is also typical of results on several other specimens taken from the same original sample, consists of six lines centred about $g = 2$ with a total width of about 500 gauss. The form of this spectrum is similar to that to be expected from a Mn^{2+} ion in a cubic environment, the splitting arising from an isotropic hyperfine interaction with $I = \frac{5}{2}$ (Low, 1953). At this resolution it is closely similar to the results of Baker *et al.* (1958) using synthetic $CaF_2(Mn)$.

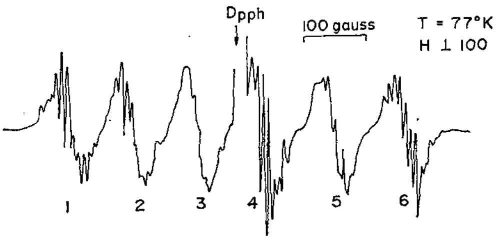

FIG. 1. The resolved hyperfine and superhyperfine structure of the e.s.r. spectrum in the Broken Hill fluorite at 77 °K. The lines are numbered in order of increasing magnetic field. The break in the fourth line is the location of the DPPH marker resonance.

Clear evidence of structure is visible on some of these lines, and on further increasing the resolution each of the six peaks was observed to consist of several well-resolved superhyperfine lines resulting from the interaction of the $3d$ electrons with the surrounding fluorine nuclei. The superhyperfine splitting gave in general eight or nine components to each of the six hyperfine lines of the spectrum as may be seen from fig. 1. This type of spectrum has been observed previously by Vinokurov and Steponov (1964) and Van Gorkom (1970) in synthetic materials, but to our knowledge this is the first time that it has been seen in natural CaF_2.

It is generally accepted that the Mn^{2+} ion enters the lattice substitutionally at a Ca^{2+} site, with the normal nearest-neighbour fluorine ions all present. The e.s.r. spectrum may then be defined by the spin hamiltonian

$$\mathscr{H} = g\beta H.s+\tfrac{1}{6}a[S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)]+ \\ +AS.I+g_n\beta_n H.I+\sum_j A'_j S.I_j, \quad (1)$$

where the first two terms give the fine-structure energy levels (the splitting of these is not readily observed in the present work), A is the hyperfine coupling constant and A'_j the superhyperfine coupling constant between the ionic spin S and the nuclear spin I_j of the jth nearest neighbour.

Using first-order perturbation theory, the $|\Delta m| = 1$ e.s.r. transitions are given by

$$h\nu = g\beta H+\tfrac{35}{120}a[m_s^4-(m_s-1)^4-\tfrac{95}{14}(m_s^2-(m_2-1)^2)]+SHF. \quad (2)$$

The last term, SHF, is the superhyperfine splitting term, which for the interaction of an Mn^{2+} ion with a single fluorine neighbour is given by

$$SHF = [\{A'_s+A'_p(3\cos^2\theta-1)\}^2+9A'^2_p\theta\sin^2\theta]^{\frac{1}{2}}, \quad (3)$$

where A_s and A_p are the isotropic and anisotropic parts of the SHF interaction respectively and θ is the angle between the magnetic field and the line joining the two ions.

By examining the angular dependence of the spectrum it has been possible to evaluate the various terms in equations 1 and 3, with the exception of a, which is known to be small in this system (Van Gorkom, 1970). These values, along with the g value, are given in Table I, where the results from synthetic crystals are also shown.

In some of the lines of the spectrum it was just possible to resolve some of the five ($S = \frac{5}{2}$) fine structure lines from which the estimate of a was obtained that is given in Table I. It is evident from this table that the manganese ions in this natural CaF_2 sample have entered the lattice substitutionally into a Ca^{2+} site, with an undisturbed nearest-neighbour environment. A second type of site has been identified by Van Gorkom (1970) using electron spin and electron nuclear double resonance methods, in which the substitutional site is surrounded by oxygen nearest neighbours forming either an $(MnO_6)^{10-}$ or an $(MnO_8)^{14-}$ complex.

TABLE I. *A comparison of the different terms of equation (1) for natural and synthetic* $CaF_2(Mn)$, *at 77 °K.*

	g	A $10^{-4}\,cm^{-1}$	A_s $10^{-4}\,cm^{-1}$	A_p $10^{-4}\,cm^{-1}$	a $10^{-4}\,cm^{-1}$
Present sample	2·002	94·5±2·1	5·5±1·4	3·95±0·7	0·7±0·1
Synthetic CaF_2:Mn (van Gorkom, 1970)	2·002	96·0	8·8	2·7	0·6*

* At 295 K.

The charge compensation at this site is far away from the centre, since the e.s.r. spectrum retained its cubic symmetry and the $(MnO_6)^{10-}$ site was favoured because of the known stability of the Mn^{2+} ion in sixfold coordination. The characteristics of the e.s.r. spectrum of this second site are very different from the simple site, each line of the six-line spectrum consisting of only five fine structure lines in this case, with no superhyperfine structure visible. There was, however, no evidence for the existence of this Mn–O complex in this sample.

We must conclude, therefore, that during the deposition of the fluorite presently being investigated conditions were such as to favour the formation of the substitutional manganese site surrounded by the normal complement of fluorine ions rather than by a shell of oxygen neighbours. Whether this is also the case in the other fluorites for which the Mn^{2+} resonance has been observed is not yet known, but it would be interesting to examine these specimens further in an attempt to detect the spectrum of the Mn–O complex in natural CaF_2.

REFERENCES

BAKER (J. M.), BLEANEY (B.), and HAYES (W.), 1958. *Proc. Roy. Soc.* **247**, 141.
HUNT (R. P.), SMITH (F. W.), and TAYLOR (K. N. R.), 1973. To be published.
LOW (W.), 1953. *Phys. Rev.* **105**, 793.
MACKENZIE (K. J. D.) and GREEN (J. M.), 1971. *Min. Mag.* **38**, 459–70.

PRZIBRAM (K.), 1956. *Irradiation colours and luminescence*, Oxford (Pergamon).
SCHULMAN (J. H.) and COMPTON (W. D.), 1963. *Color centres in solids*, Oxford (Pergamon).
VAN GORKOM (G. G. P.), 1970. *Journ. Phys. Chem. Solids*, **31**, 905.
VINOKUROV (V. N.) and STEPONOV (V. G.) [Винокуров (В. Н.) и Степонов (В. Г.)], (1964), *Sov. Phys.* (*Solid State*) **6**, 303.

[*Manuscript received 10 April 1973; revised 10 October 1973*]