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ELECTRON PARAMAGNETIC RESONANCE OF VANADIUM AND CHROMIUM IN CaF_2

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In the overwhelming majority of cases in compounds studied by the e.p.r. method, the nearest environment of paramagnetic ions is a distorted octahedron. Studies of elements of the iron group in matrices where the ligand atoms form a cube or tetrahedron are of considerable interest. Upon isomorphous incorporation into lattices of the fluorite type, paramagnetic atoms should be surrounded by 8 fluorine ions.

After a number of unsuccessful attempts to dope CaF_2 with elements of the iron group, we succeeded, by saturating the melt with fluorine, in isomorphously introducing vanadium and chromium into the CaF_2 lattice.*

In crystals containing vanadium, at 77° K e.p.r. spectra are observed that are due to two types of vanadium ions. The spectrum of type I ions is isotropic –one group of lines consisting of 8 hyperfine components ($g = 1.933$, $|A| = 263 \pm 2$ MHz). A study of the angular dependence of the spectrum of type II centers shows that 4 vanadium ions are in electric fields of axial symmetry. The z axes of these fields are directed along the body diagonals of the unit cell of the crystal. The e.p.r. spectrum of each of the 4 ions is described by a spin Hamiltonian of axial symmetry with $s = 3/2$ ($b_2^0 = 42.31 \pm 0.05$ GHz, $g_\parallel = 1.935 \pm 0.005$, $g_\perp = 1.943 \pm 0.005$, $|A| = 237 \pm 1$ MHz, $|B| = 277 \pm 3$ MHz). Lowering the temperature to 4.2° K does not qualitatively change the spectrum pattern. By varying the growth conditions, it was possible to obtain samples containing only type I or type II centers.

Analysis of these data and comparison with the expected e.p.r. spectra of V^{2+}, V^{3+}, V^{4+} ions lead to the following conclusion: type I ions are V^{3+}; type II ions are V^{2+}.

The ground state of the V^{3+} ion in an electric field of cubic symmetry (coordination number 8) is an orbital singlet, whose threefold spin degeneracy is retained. Therefore, one isotropic group of hyperfine components with a g-factor smaller than 2.0023 should be observed. The value of A correlates with the spin-orbit coupling constant of the Co^{2+} ion in CaF_2 ([2]). The comparatively short spin-lattice relaxation time, which does not allow the effect to be observed at room temperature, is probably due to the smaller splittings in the crystal field (in comparison with octahedral coordination).

The main argument in favor of the type II ions being V^{2+} is the value of the electron spin $s = 3/2$ of the lower energy level. The ground state of the V^{2+} ion in a crystal field is an orbital triplet. As is known, in such cases one may expect manifestation of the Jahn–Teller effect. For octahedral coordination it has been shown (see, for example, ([3])) that this effect can lead to the creation of stable distortions along third-order axes. On the basis of symmetry considerations, a similar distortion, leading to the appearance of a trigonal component of the crystal field, should also be expected for coordination number 8. The trigonal com-

* The first attempt to introduce elements of the iron group into CaF_2 was made in ([1]).

component splits the lower orbital level into a singlet and a doublet. Taking the spin-orbit interaction into account leads to the splitting of the spin quartet state of the orbital singlet into two Kramers doublets with an interval $2b_2^0$. Calculations show that the g-factors of such a system of levels must be less than 2.0023. Thus, one of the reasons for the existence of trigonal V^{2+} centers in CaF_2 may be the Jahn—Teller effect.

In crystals containing V^{3+}, the principle of local compensation of excess charge is not fulfilled. However, the introduction of positive compensators (Ag, Cu) into the melt increases the intensity of the spectrum by a factor of 10–15. Positive compensators do not affect the V^{2+} spectrum.

The general pattern of the EPR spectrum in crystals containing chromium is analogous (without hyperfine structure) to that described above for V^{2+}. Therefore we believe that the ions responsible for the effect are Cr^{3+}, for which $|b_2^0| = 59.4 \pm 0.2$ GHz, $g_\parallel = 1.961 \pm 0.005$, $g_\perp = 1.97 \pm 0.01$.

It should be noted that in all cases an additional structure is observed, apparently caused by the interaction of paramagnetic ions with the magnetic moments of fluorine nuclei.

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Note: Figure translations are in progress. See original paper for figures.