Paramagnetic Resonance of Transition Metal Ions in Unusual Valence States

W. HAYES

Clarendon Laboratory, Oxford, England

Valence changes of magnetic impurities in crystals are produced by x-irradiating the crystals. The valence changes are detected using ESR techniques.

1. Introduction

It is possible to produce transition ions in metastable valence states by introducing them into suitable host lattices as impurities and subsequently exposing the crystals to ionising radiations. The impurities may trap electrons or holes released during the irradiation and hence change their valence states. The irradiation induced valence changes can be annealed out by heating the crystals. We shall concern ourselves here with iron group ions in NaF and LiF, silver in KC1 and thulium in CaF_2. A change in the valence state of a magnetic ion may produce large nuclear isomeric shifts which in some cases can be investigated using the recoilless resonance absorption of γ quanta[1].

2. Iron Group Impurities in LiF and NaF

When iron group ions are introduced into LiF and NaF as impurities they normally enter the lattice substitutionally in the divalent form. During x-irradiation at room temperature the impurity ions trap electrons and are subsequently observed by ESR methods in the monovalent form; the ions Cr II, Fe II, Co II and Ni II have been found in NaF and Fe II and Ni II in LiF. The ESR spectra of the monovalent ions in NaF have been briefly described[2,3,4]. Wilkens[5] has recently investigated these systems with special emphasis on Ni II.

Ni II ($3d^9$, ^2D) is isoelectronic with Cu III and in an octahedral cubic crystal field has an orbital doublet (x^2-y^2, $3z^2-r^2$) lowest. In such a situation we may get a Jahn-Teller[6] distortion which raises the orbital degeneracy. In NaF we observe two spectra with tetragonal symmetry, I (Table I) with the state x^2-y^2 lowest and II (Table I) with the state $3z^2-r^2$ lowest; the former is due to an extension of the surrounding fluorine octahedron along $\langle 100 \rangle$ and the latter a compression along $\langle 100 \rangle$. To account for the observed g-values and fluorine h.f.s. it is necessary to postulate an admixture of x^2-y^2 into $3z^2-r^2$ and it has been pointed out by Dr. M.C.M. O'Brien (private communication) that this may be achieved by zero point lattice vibrations.

The superscript I on the fluorine h.f.s. constants refers to the four fluorines in the plane perpendicular to the symmetry axis (z) and the superscript II to the two fluorines on the symmetry axis. The fluorine h.f.s. constants are given in units of 10^{-4} cm^{-1}.

3. Silver in KC1

An investigation of the ESR and optical absorption spectra of x-irradiated KC1 : Ag has been carried out by Delbecq, Hayes, O'-Brien and Yuster (to be published). Irradiation in a microwave cavity at 77°K produces silver atoms, Ag I, and Cl_2^- hole centres[7]. Silver enters the KC1 lattice substitutionally in the monovalent form, Ag II, and traps electrons during the irradiation forming Ag I which has the configuration $4d^{10} 5s$, ^2S. There are two naturally occurring isotopes, ^{107}Ag (51%) and ^{109}Ag (49%) each with $I=1/2$.

Table I. Constants of the ESR Spectrum of Monovalent Nickel.

Spectrum	$g_{\parallel}$	$g_{\perp}$	A_x^{I}	A_y^{I}	A_z^{I}	$A_{x,y}^{\mathrm{II}}$	A_z^{II}
I	2.776	2.116	67.0	29.6	24.8	11.6	7.6
II	2.067	2.464	24.0	24.0	15.0	48.0	184.0

The spectra from the two isotopes overlap because of an extensive resolved chlorine h.f.s. A set of measurements was made by growing a crystal containing enhanced ^{109}Ag (99.9%) and we find $g=2.003\pm0.003$ and $A=0.0639\pm0.0002$ cm^{-1}.

When the crystals which had been irradiated at 77°K are warmed to 208°K, a glow is observed. Examination of the ESR spectrum after extinction of the glow shows that the Cl$_2^-$ hole centres have disappeared and a new centre, Ag III, is observed due to trapping of holes at Ag II sites. Ag III has the ground state $4d^9$, ^2D and like Ni II ($3d^9$, ^2D) is a Jahn-Teller ion. A distortion occurs along $\langle 100 \rangle$ leaving the x^2-y^2 orbital lowest and we observe bonding with the four chlorines in the plane perpendicular to the symmetry axis. The spectrum may be fitted with $g_{\parallel}=2.193$, $g_{\perp}=2.035$, $A=38\times10^{-4}$ cm^{-1}, $B=30\times10^{-4}$cm^{-1}, $A'=5\times10^{-4}$cm^{-1} and $B'=30\times10^{-4}$cm^{-1} where A and B describe the silver h.f.s. and A' and B' the chlorine h.f.s.

Upon heating the crystal to 100°C, Ag I and Ag III mutually annihilate each other.

4. Thulium in CaF$_2$

When rare earth ions are introduced as impurities into CaF$_2$ they normally enter the lattice in the trivalent form on substitutional sites and charge compensation may be achieved by a F$^-$ ion in a nearest interstitial site[3],[9]. However, charge compensation may be remote in which case the ESR spectrum shows the cubic symmetry of the CaF$_2$ lattice[10].

When unirradiated single crystals of CaF$_2$: Tm are examined down to 20°K no resonance is observed. After x-irradiation at room temperature an isotropic ESR spectrum with a two line h.f.s. is observed at 77°K with $g=3.453\pm0.003$ and $A=368\pm2\times10^{-4}$cm^{-1}. The spectrum is assigned to Tm III ($4f^{13}$, $^2F_{7/2}$). It appears that Tm IV ions on cubic laittce sites capture electrons during the irradiation forming Tm III ions and the latter do not anneal appreciably until the crystal is heated to about 550°C. The g and A values of Tm III have been considered in detail by Hayes and Twidell[11].

References

1 R. T. Mossbauer: Z. Physik **151** (1958) 124.
2 B. Bleaney and W. Hayes: Proc. Phys. Soc. **B70** (1957) 626.
3 W. Hayes and D. A. Jones: Proc. Phys. Soc. **71** (1958) 503.
4 W. Hayes: Discussions of the Faraday Soc. **26** (1958) 58.
5 J. Wilkens: Thesis, Oxford (1961).
6 H. A. Jahn and E. Teller: Proc. Roy. Soc. **A161** (1937) 220.
7 T. Castner and W. Känzig: J. Phys. Chem. Solids **3** (1957) 178.
8 B. Bleaney, P. M. Llewellyn and D. A. Jones: Proc. Phys. Soc. **B69** (1956) 858.
9 J. M. Baker, W. Hayes and M. C. M. O'Brien: Proc. Roy. Soc. **A254** (1960) 273.
10 E. Friedman and W. Low: J. Chem. Phys. **33** (1960) 1275.
11 W. Hayes and J. W. Twidell: J. Chem. Phys., **35** (1961) 1521.

DISCUSSION

J. Kanamori: Have you observed the transition from tetragonal symmetry to cubic symmetry in the resonance pattern of Ag^{++} when the temperature is raised?

W. Hayes: We have not observed an isotropic Ag III resonance because relaxation broading smears out the lines before the onset of the isotropic resonance.