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ESR STUDIES OF ELECTRON IRRADIATED $K_3Ir^{III}(CN)_6$ IN KCl SINGLE CRYSTALS II - STRONG QUADRUPOLE EFFECTS ON THE HYPERFINE STRUCTURE IN $Ir^{II}(CN)_5$ SPECIES

by

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ABSTRACT

The effects of a large quadrupolar interaction in the $Ir^{II}(CN)_5$ molecule in a KCl lattice are analyzed using a MAGNSPEC computer program. Some empyrical rules are given to help in the interpretation of this kind of spectra. g and A deduced ligand field formulae for a d_{z^2} ground state are used to calculate the unpaired electron density on the metal. The hyperfine constants are determined to be positive leading to a positive value for the core polarization constant χ, indicating a mixture of 6s wave function in the unpaired electron molecular orbital. The ESR data indicate the presence of two non-equivalent sites for the $Ir^{II}(CN)_5$ molecule in KCl, differing only by the orientation of the principal axes of the quadrupolar interaction. A possible influence of the vacancies created by charge compensation on the existence of these two sites is discussed. The ratio between the nuclear quadrupole moments for the iridium isotopes is determined to be

$$^{193}Q: {}^{191}Q = 0.91 \pm 0.03$$

INTRODUCTION

Spin Hamiltonians, introduced by A. Abragam and M. H. L. Pryce[1], are a very powerful tool in interpreting ESR spectra and in relating experiment with theory. For an effective spin S = 1/2, neglecting nuclear Zeeman interaction, we can write a Spin Hamiltonian as follows:

$$\mathcal{H} = \beta\, \vec{H}\cdot\vec{\vec{g}}\cdot\vec{S} + \vec{S}\cdot\vec{\vec{A}}\cdot\vec{I} + \vec{I}\cdot\vec{\vec{P}}\cdot\vec{I}$$

The three terms represent, respectively, an electron Zeeman, a hyperfine and a quadrupolar interaction.

In almost all experiments reported up to now the quadrupolar term is very small compared to the hyperfine term and we can use Bleaney's perturbation theory formulae [2] for the cases with axial symmetry or Golding's for the more general case [3]. In 1968, H. van Willigen and J. G. M. van Rens reported the single crystal ESR spectra of Au(II) diethyldithiocarbamate which show the gold ESR quarted flanked by pairs of satellites, this quartet displayed in a very peculiar form: the lines in the perpendicular spectra are not equal ly spaced with the central lines lying very close together. These features are ascribed to the effect of a large electric quadrupole interaction comparable to the hyperfine interaction. This effect appears when the metal atom combines a small magnetogyric ratio with a relatively large quadrupole moment and we shall call it strong quadrupole interaction (SQI) from now on.

Among the nuclei which could present a SQI, besides ^{167}Er and ^{235}U, the stable iridium 193 and 191 isotopes are the most probable, once, of course, they are placed in a site with a non - zero electric field gradient.

These isotopes, both with nuclear spin I = 3/2, have a natural abundance

of 61.5% and 38.5%, respectively. Iridium 191 has a magnetic moment [7] of (0.1453 ± 0.0006) β_N and a nuclear electric quadrupole moment of about 1.5 barn [8]. Iridium 193 has a magnetic moment of (0.1583 ± 0.0006) β_N and a nuclear electric quadrupole moment of about 0.92 ± 0.09 times the value for the other isotope [9].

ESR spectra presenting a SQI are not easy to interpret. There are no analytical formulae available and numerical methods must be employed to diagonalize the Spin Hamiltonian matrix. To our knowledge, the best way to do it is to use a computer program like MAGNSPEC [5] and deal with the principal values of the Spin Hamiltonian tensors through a laborious trial method. Additional complications arise when the principal axes of the tensors are not coincident.

This paper is concerned with the SQI spectra of $Ir^{II}(CN)_5$ in a KCl lattice. This molecule presents a d^7 unpaired electron in a d_{z^2} antibonding orbital. This and the superhyperfine structure with the CN ligands have been discussed in a previous paper [6].

EXPERIMENTAL

The crystal growing method, the equipment and irradiation techniques are the same as described in reference 6. The fitting of the ESR spectra has been done with an IBM 370/145 computer using a MAGNSPEC program.

RESULTS

The $Ir^{II}(CN)_5$ molecule presents an almost axial symmetry.

The measured g values, the components of the hyperfine interaction tensor and the components of the quadrupolar tensor are shown in table I, as well as their polar angles referred to a coordinate system coincident with the KCl principal axes with Z along the non-equivalent CN of the molecule [6].

Table I shows at least three striking features. First, the values of the quadrupolar tensor are comparable to the values of the hyperfine tensor. Second, the principal axes of the quadrupolar tensor do not coincide with the principal axes of the g and A tensors. Third, there are two non-equivalent sites for $Ir^{II}(CN)_5$ in the KCl host lattice, differing only by the orientations of the principal axes of the tensor P. We shall call these sites A and B.

The parallel ESR spectrum is not very affected by the SQI and approximate values of A_Z and g_Z can be obtained directly from the spectrum.

Fig. 1 shows the superimposed X and Y ESR spectra of $Ir^{II}(CN)_5$ in KCl with the MAGNSPEC theoretical reconstitution. The Q-band is used in order to diminish the overlap between the spectra. Unfortunately we loose resolution at the Q-band because we have experimental difficulties in lowering the temperature of the sample. Ligand superhyperfine structure has not been plotted in order to avoid crowding the figure. X and Y are tipical SQI ESR spectra: the central quartet strong lines are very close together and there are satellites flanking the spectrum. The lines at-

tributed to sites A and B are almost coincident, their separation being smaller than the line width.

The X-band perpendicular spectrum at 45^{o} is shown in Fig. 2 with the MAGNSPEC theoretical reconstitution. The number of lines at this position is a minimum because the X and Y spectra coincide. This spectrum is symmetrical about its center and the amplified low field satellites are shown in this figure. The lines attributed to sites A and B are clearly resolved: the intense outer peaks coincide but the peaks of the middle do not coincide. Intensities are in good agreement with this assignement. Satellites are well resolved and are not one but two pairs of lines for each site. We must remember that each line is further split in a triplet by the superhyperfine interaction.

SOME EMPYRICAL RULES AND INTERPRETATION OF THE SQI ESR SPECTRA

As mentioned in the Introduction, ESR spectra presenting a SQI are not easy to interpret. From our experience with MAGNSPEC we can, however, try to state some approximate rules about the influence of a single Spin Hamiltonian parameter on the SQI ESR spectra. More details will be given in ref. 10. These rules for an effective spin 1/2 interacting with a spin 3/2 nucleus are:

a) approximate values of the g tensor components can be measured directly from the center of the corresponding spectra.

b) the spacing between outer central lines varies linearly with the corresponding component of the hyperfine tensor. This

variation influences the middle central lines in a smaller proportion.

c) the spacing between outer central lines and middle central lines varies linearly with η, the quadrupole asymmetry parameter. If η increases the former spacing decreases and the latter increases.

d) if $\Theta_{zz} = 0$, i.e., the Z principal axis of the quadrupolar interaction coincides with the Z axis of the g and A tensor, even if the X and Y axes do not coincide, the strong lines are flanked by pairs of satellites. The distance in gauss between the lines of a pair gives a fairly approximate value for the corresponding component of the hyperfine interaction tensor. If $\phi_{xx} = 0^{o}$, the middle central lines of the perpendicular spectrum at 45^{o} practically coincide. If $\phi_{xx} = 45^{o}$ the X and Y middle central lines practically coincide. For intermediate ϕ_{xx} values these lines do not coincide for $\eta \neq 0$.

e) the distance in gauss from the satellite lines to the center of the spectrum is linearly dependent on the P_z value. In our case a variation of 10^{-4} cm^{-1} in P_z causes a change of about 2.2 gauss in the position of the satellites. The intensities of these lines increase with decreasing P_z.

f) if $\Theta_{zz} \neq 0$ each line of the satellite pairs is split into two lines of unequal intensity. The sum of these intensities remain constant when Θ_{zz} is varied. The middle central lines spacing increases with Θ_{zz} but the outer central lines are only slightly influenced.

As can be seen from the figures 1 and 2, our interpretation of the ESR spectra of $Ir^{II}(CN)_5$ is in good agreement with the empyrical rules formulated above. These rules by no means eliminate the laborious trial method of fitting the spectra. They only diminish and somehow organize the work. It can be seen from these rules that the influence of the parameters η and Θ_{zz} are closely related. This puts some degree of unaccuracy in the determination of these parameters for sites A and B. We did assume that they have the same asymmetry parameter η.

The measured values of the quadrupolar interaction tensor with iridium 193 and iridium 191 give the following ratio of the iridium nuclear quadrupole moments:

$$^{193}Q: {}^{191}Q = 0.91 \pm 0.03$$

This agrees with the ENDOR value of 0.92 ± 0.09 given by J. J. Davies and J. Owen [9].

DISCUSSION

g VALUES AND HYPERFINE INTERACTION

In reference 6 we assumed an axial symmetry for the $Ir^{II}(CN)_5$ molecule and we used Mc Garvey's formulae [11] for relating the measured g values with the ligand field theory. Rededucing Mc Garvey's formulae for the hyperfine interaction we did conclude that they are not completely correct.

For a C_{4v} low spin d^7 system with an unpaired electron in a d_{z^2} orbital ($^2A_1$ ground configuration), there will be a mixture via spin-

orbit coupling with a ^2E excited configuration. The $|E'\ \alpha'>$ components of the Kramer's doublets for these two configurations, in the complementary scheme, are $|b_1^2\ a_1^+>$ and $|b_1^2\ (1)^->$ respectively. Assuming a LCAO-MO scheme the corresponding anti-bonding orbitals can be written:

$$a_1 = \alpha\ \underset{\sim}{a}_1 - \alpha' \psi_{a_1}$$

and

$$(1) = \beta(\underset{\sim}{1}) - \beta'\ \psi_{L_1}$$

ψ_{a_1} and ψ_{L_1} are linear combinations of the ligand orbitals of appropriate symmetry. The symbol $\sim$ indicates an atomic orbital.

Without the use of perturbation theory the formulae for the g values and hyperfine interaction are:

$$g_{||} = g_o \cos 2\Theta + 2k'' \sin^2 \Theta$$

$$g_{\perp} = g_o \cos^2 \Theta + \sqrt{6}\ k' \sin 2\Theta$$

$$A_{||} = \left[-\kappa + \frac{4}{7}\alpha^2 \cos^2\Theta + \frac{12}{7}\beta^2 \sin^2\Theta + \frac{\sqrt{6}}{7}\alpha\beta \sin 2\Theta\right]P$$

$$A_{\perp} = \left[-\kappa - \frac{2}{7}\alpha^2 \cos^2\Theta - \frac{6}{7}\beta^2 \sin^2\Theta - \frac{15}{14}\sqrt{6}\,\alpha\beta \sin 2\Theta\right]P$$

The orbital reduction factors k' and k" are defined by the following expressions:

$$k' = <(1)|\ell_+|a_1>/\sqrt{6} = \alpha\beta - \alpha\beta' S_e - \alpha'\beta S_{a_1} + \frac{\alpha'\beta'}{\sqrt{6}} < \psi_{L_1}|\ell_+|\psi_{a_1}>$$

$$k'' = <(1)|\ell_z|(1)> = 1 - \beta'^2 (1 - <\psi_{L_1}|\ell_z|\psi_{L_1}>)$$

S_e and S_a are the overlap integrals $\langle (\underline{1})|\psi_L\rangle$ and $\langle a_1|\psi_{a_1}\rangle$ respectively. The angle Θ is such that:

$$\tan\Theta = \frac{\sqrt{6}\,k'\,y}{1 + yk''/2}, \quad \text{where } y = \frac{\lambda}{E_2 - E_1}$$

κ is the isotropic contact constant and $P = g_o\, g_N\, \beta\beta_N \langle r^{-3}\rangle$.

The sign of λ, the spin-orbit coupling constant, has already been changed to give the right expressions for d^7, not d^3.

To use the formulae above we must approximate the experimental data given in table I to axial symmetry. This can be done by setting $g_\perp = 2.2063$, $g_{||} = g_z$, $A_\perp = 20.5 \times 10^{-4}\ cm^{-1}$ and $A_{||} = A_z$. Changing k'' and β from 1.0 to 0.80, the experimental values can be fitted with $|\alpha|^2 = 0.50 \pm 0.05$, $k' = 0.37 \pm 0.02$, $\Theta = 7.3^o \pm 0.3$ and $y = 0.32 \pm 0.4$. The small value of $|\alpha|^2$ is an evidence of a large delocalization of the unpaired 5d electron on the ligands, giving rise to the superhyperfine structure reported previously[6]. The positive combination of signs for the hyperfine interaction is the only possible combination which gives an acceptable value for $|\alpha|^2$. In the calculations we have used the value $\langle r^{-3}\rangle = 10.9479$ a.u. calculated in reference 12 for a $5d^7$ Ir^{2+} ion.

The core polarization field per unpaired spin, χ, can be calculated from the Fermi contact term κ by the formula

$$\chi = -\frac{3}{2}\kappa \langle r^{-3}\rangle$$

From our experimental data $\chi = +18.5 \pm 0.5$ a.u. A. J. Freeman et al.[13] calculated by means of the spin - unrestricted Hartree - Fock method values of χ for divalent 5d ions. Their values are -17.5 ± 0.5 a.u. Our large and positive χ value only can be explained if we admit a mixture of the 6s wave

function in the unpaired electron molecular orbital; this would give rise to a positive contribution to the isotropic hyperfine interaction. This mixture is expecte since the ground-configuration transforms as A_1, the totally symmetric irreducible representation of the symmetry group of the molecule.

ELECTRIC FIELD GRADIENT AT Ir NUCLEUS. SITES A AND B

It is generally accepted that the electric field gradient (EFG) on the metal atom of a complex is the sum of a valence EFG and a smaller contribution due to the lattice. It is also generally accepted that the valence contribution q_{val} is decreased by the Sternheimer shielding factor and the lattice contribution q_{Lat} is enhanced by the Sternheimer antishielding factor. For an unpaired electron in a d_{z^2} orbital, neglecting spin-orbit contributions, q_{val} can be written as follows:

$$q_{val} = -\frac{4}{7} < r^{-3} > (1-R)|\alpha|^2$$

Assuming the Sternheimer shielding factor $(1-R) \approx 0.6$ we calculate $q_{val} \approx -18.2 \times 10^{17}$ V/cm^2. The corresponding P_z value is about -17×10^{-4} cm^{-1}. Comparing this value with the experimental $|P_z| = 20.3 \times 10^{-4}$ cm^{-1} it seems reasonable to think that in the $Ir^{II}(CN)_5$ molecule the predominant contribution to the total EFG is provenient from q_{val}, implying in a negative value for the experimental P_z.

From table I it can be seen that the $Ir^{II}(CN)_5$ molecule can occupie two different sites in the KCl lattice. These sites differ only by the orientation of the principal axes of the quadrupolar interaction (we did assume equal η for A and B). This result strongly suggests that the two

There are also other tendencies that I was not able to touch upon, such as the study of infinite dimensional analytic geometry carried on by Douady, Ramis and Ruget; or of infinite dimensional analytic manifolds; or applications of complex analysis in infinite dimensions to physics; etc.

In all these areas, the problems outnumber the solutions.

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TABLE I

SPIN HAMILTONIAN PARAMETERS *. A AND P IN 10^{-4} cm^{-1}

	xx	Θ	ϕ	yy	Θ	ϕ	zz	Θ	ϕ
g [a]	2.2103	0.0	0.0	2.2022	0.0	0.0	1.9665	0.0	0.0
A^{193} [b]	(+)20.3±0.5	0.0	0.0	(+)20.7 0.5	0.0	0.0	(+)51 ± 1	0.0	0.0
P^{193}site A [b]	(+)10.6±0.4	95±2	30±5	(+)11.7±0.4	93±2	120±5	(-)22.3±0.3	6±2	60±5
P^{193}site B [c]	(+)10.6±0.4	92±2	30±5	(+)11.7±0.4	91±2	120±5	(-)22.3±0.3	2±2	60±5

* The signs in parentheses have been predicted by theory and have not been determined experimentally.

a - g_x and g_y values are slightly different from that reported in ref. 6. They have been adjusted during the fitting. Experimental errors have been reconsidered and are ± 0.0007.

b - Values for the hyperfine interaction with ^{191}Ir can be obtained by dividing these values by 1.089, the ratio between the magnetic moments of ^{193}Ir and ^{191}Ir.

c - Values for the quadrupolar interaction with ^{191}Ir can be obtained by dividing these values by 0.91. This will be discussed in the text.

* * *

11. S. Baryton, Fonctions A-analytiques, Comptes Rendus de l'Academie des Sciences de Paris 270 (1970), 1586-88.

12. J. Bochnak, Analytic Functions in Banach Spaces, Studia Mathematica 35 (1970), 273-292.

13. J. Bochnak et J. Siciak, Fonctions Analytiques dans les Espaces Vectoriels Topologiques Réels ou Complexes, Comptes Rendus de l'Académie des Sciences de Paris 270 (1970), 643-646.

14. J. Bochnak and J. Siciak, Remarks on Domains of Holomorphy in Topological Vector Spaces, Bulletin de l'Académie Polonaise des Sciences 19 (1971), 9-12.

15. J. Bochnak and J. Siciak, Polynomials and Multilinear Mappings in Topological Vector Spaces, Studia Mathematica 39 (1971) 59-76.

16. J. Bochnak and J. Siciak, Analytic Functions in Topological Vector Spaces, Studia Mathematica 39 (1971), 77-112.

17. P. J. Boland, Espaces Pondérés de Fonctions Entières et de Fonctions Entières Nucléaires sur un Espace de Banach, Comptes Rendus de l'Académie des Sciences de Paris 275 (1972), 587-590.

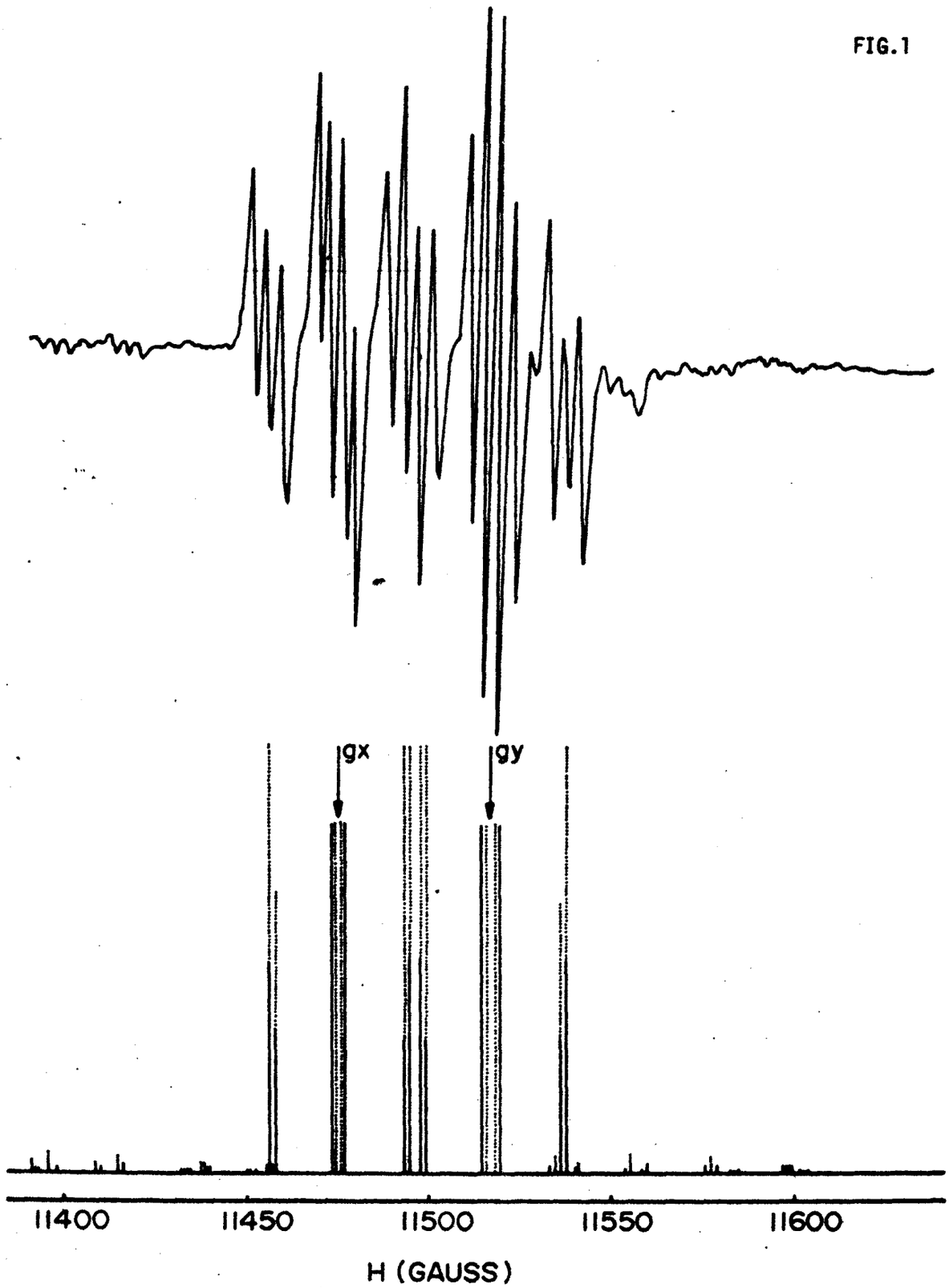
18. P. J. Boland, Some Spaces of Entire and Nuclearly Entire Functions on a Banach Space, Journal fur die Reine and Angewandte Mathematik, to appear in two parts.

19. N. Bourbaki, Variétés Différentielles et Analytiques, Fascicule de Résultats, Hermann, France, 1-7 (1967) and 8-15 (1971).

20. H. J. Bremermann, Holomorphic Functionals and Complex Convexity in Banach Spaces, Pacific Journal of Mathematics 7 (1957), 811-831.

21. H. J. Bremermann, The Envelopes of Holomorphy of Tube Domains in Infinite Dimensional Banach Spaces, Pacific Journal of Mathematics 10 (1960), 1149-1153.

FIG.1



32. G. Coeuré, Fonctions Plurisousharmoniques sur les Espaces Vectoriels Topologiques et Applications à l'Étude des Fonctions Analytiques, Annales de l'Institut Fourier 20 (1970), 361-432.

33. G. Coeuré, Fonctionnelles Analytiques sur Certains Espaces de Banach, Annales de l'Institut Fourier 21 (1971), 15-21.

34. G. Coeuré, Prolongement Analytique en Dimension Infinie, Symposium of Analysis, Recife 1972, Lecture Notes in Mathematics, Springer-Verlag, Germany, to appear.

35. G. Coeuré, Espaces Normés σ-Complets, Colloque d'Analyse, Rio de Janeiro 1972, Hermann, France, to appear.

36. J. F. Colombeau, Quelques Exemples Singuliers d'Applications G-Analytiques et Différentiables en Dimension Infinie, Comptes Rendus de l'Academie des Sciences de Paris 273 (1971), 158-160.

37. J. F. Colombeau et D. Lazet, Sur les Théorèmes de Vitali et de Montel en Dimension Infinie, Comptes Rendus de l'Académie des Sciences de Paris 274 (1972), 185-187.

38. J. F. Colombeau, Sur les Applications G-Analytiques et Analytiques en Dimension Infinie, Séminaire Pierre Lelong 1971/1972, Lecture Notes in Mathematics, Springer-Verlag, Germany, to appear.

39. S. Dineen, Topologie de Nachbin et Prolongement Analytique en Dimension Infinie, Comptes Rendus de l'Academie des Sciences de Paris 271 (1970), 643-644.

40. S. Dineen, Holomorphic Functions on a Banach Space, Bulletin of the American Mathematical Society 76 (1970), 883-886.

41. S. Dineen, The Cartan-Thullen Theorem for Banach Spaces, Annali della Scuola Normale Superiore di Pisa 24 (1970), 667-676.

42. S. Dineen, Bounding Subsets of a Banach Space, Mathematische Annalen 192 (1971), 61-70.

REFERENCES

1. A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. A205, 135 (1951).

2. B. Bleaney, Phyl. Mag. 42, 441 (1951).

3. R. M. Golding, Applied Wave Mechanics, D. van Nostrand (1969).

4. H. van Willigen and J. G. M. van Rens, Chem. Phys. Letters 2, 283 (1968).

5. J. H. Mackey, M. Kopp, E. C. Tynan and Teh Fu Yen, ESR of Metal Complexes, edited by Teh Fu Yen (Plenum, New York, 1969), p. 33.

6. N. V. Vugman, R. P. A. Muniz and J. Danon, J. Chem. Phys. 57, 1297 (1972).

7. A. Narath, Phys. Rev. 165, 506 (1968).

8. Varian Associated "NMR Table", fifth edition.

9. J. J. Davies and J. Owen, J. Phys. C (Solid St. Phys.) 2, 1405 (1969).

10. N. V. Vugman, S. I. Zanette and A. O. Caride, to be published.

11. B. R. Mc Garvey, J. Phys. Chem. 71, 51 (1967).

12. L. W. Panek and G. J. Perlow, Hartree-Fock Self-Consistent Calculations of Iridium, (Argonne National Laboratory, Argonne, Illinois, 1969), report nº ANL - 7631.

13. A. J. Freeman, J. V. Mallow and P. S. Bagus, J. Appl. Phys. 41, 1321 (1970).

14. Llewellyn Jones, J. Chem. Phys. 36, 1400 (1962).

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