

X-RAY SPECTROSCOPIC AND OPTICAL REFLECTANCE STUDY OF $ZnCrCoO_4$ SPINEL

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ABSTRACT

The spinel, $ZnCrCoO_4$, on which very little work has been done so far, has been studied using the x-ray diffraction, reflectance and x-ray spectroscopic methods. It has been found that the spinel is cubic with $a = 8.29$ Å. In this spinel the oxidation states of Zn ions appear to be two and that of the Co and Cr ions three. These studies show that the spinel has the ionic structure $Zn^{2+}[Cr^{3+}Co^{3+}]O_4$. The absorption bands in the reflectance spectrum are interpreted in terms of electron transition on the basis of ligand field theory. The information regarding the crystal field splitting for Cr^{3+} and Co^{3+} ions in the spinel has been obtained.

INTRODUCTION

OXIDIC spinels have attracted attention because of their interesting electrical and magnetic properties. These properties depend upon the valence state and the site distribution of the cations in the lattice of the spinel¹⁻³. The information regarding the valence state and site distribution can be obtained from Mössbauer^{4,5}, x-ray diffraction⁶, solid solution¹, electrical and magnetic^{7,8} and optical⁹⁻¹¹ studies. The crystal structure of the spinel $ZnCrCoO_4$ has been determined by us from x-ray diffraction studies. We have also attempted to determine the electronic structure of this spinel from x-ray spectroscopic and reflectance studies.

EXPERIMENTAL

The spinel was prepared by intimately mixing together under acetone, the compounds ZnO , Cr_2O_3 and Co_2O_3 in the molar ratio 2 : 1 : 1. The mixture was dried in air to remove acetone. It was then mixed with borax and was heated in a silica crucible in a furnace for about 100 hours at $1050^\circ C$. The furnace was then switched off and the sample was allowed to cool. The compound was washed with hot water. The x-ray diffraction pattern of the powdered sample was obtained on a Debye-Scherrer camera of diameter 11.46 cm using filtered cobalt radiation.

A Machlett sealed x-ray tube with a copper target was employed as a source of radiation for x-ray spectroscopic work. The experimental technique has been described in detail elsewhere^{2,12}. Reflectance spectrum of the sample was taken on Carl-Zeiss Spectrometer VSU 2 P with a $45/\theta$ geometry in the range 280 mm to 880 mm. The reflectance of the substance was measured at the room temperature against freshly prepared NaF surface.

RESULTS AND DISCUSSION

A number of measurements of the observed few intense lines were made on the x-ray diffraction pattern. The average of the observed 'd' values for the different reflecting atomic planes are given in Table I. In

this table are also given the calculated 'd' values for comparison. These data show that the compound has a spinel structure in the space group O_h^7 (or $Fd\bar{3}m$) with lattice constant $a = 8.29 \pm 0.1$ Å. In Table I are given the intensities of the various reflections which are calculated theoretically for the most probable cation distribution $Zn^{2+}[Cr^{3+}Co^{3+}]O_4$ by using the formula¹³

$$I_{hkl} \propto |F|^2 P \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta}$$

where the notations have their usual meanings. It was observed that the reflection from the 311 planes was the most intense. To this line was assigned the intensity 100. The intensities of the other reflections were calculated considering the 311 as standard. It was observed that the intensities calculated theoretically for the oxygen ion parameter $u = 0.375$ for the above cation distribution were in close agreement with the experimentally observed intensities as seen in Table I. It is therefore inferred that in this spinel the Zn^{2+} ions occupy tetrahedral sites while Cr^{3+} and Co^{3+} ions occupy octahedral sites.

TABLE I

Results of the x-ray diffraction study of $ZnCrCoO_4$

Sl. No.	d in Å		Intensity		hkl
	Obs.	Calc.	Obs.	Calc.	
1.	2.92	2.93	70	70.8	220
2.	2.50	2.50	100	100	311
3.	2.07	2.07	60	59.5	400
4.	1.58	1.59	30	27.8	511
5.	1.28	1.26	10	12.8	533

Our measurements on the x-ray absorption spectrum of the spinel gave the wavelength of the K absorption edge of cobalt as 1601.8 X.U. This value is in agreement with those reported earlier for the trivalent compounds of cobalt^{12,13}. It is concluded therefore that in the spinel cobalt is in trivalent state. Since Zn always exists in divalent state¹⁴ in this spinel

according to the charge rule, the Cr ion must exist in the trivalent state.

The reflectance curve for the spinel ZnCrCoO₄ is shown in Fig. 1. There are four absorption bands A, B, C and D occurring at 6850 Å (14600 cm⁻¹), 5800 Å (17240 cm⁻¹), 4700 Å (21275 cm⁻¹) and 3500 Å (28570 cm⁻¹) respectively. It is recognised¹⁶ that many features of the spectra of chemical entities in the solution and also in the crystals are explicable in terms of ligand field or molecular orbital (M.O.) levels. These levels are somewhat perturbed in solids. As an approximation for the solids¹⁶ it is possible to retain the configuration of atoms and molecules and obtain an intelligible picture which very often agrees with experience. We have tried to explain the reflectance spectra of ZnCrCoO₄ on the basis of the ligand field theory.

For the spin-free Co³⁺ octahedral ion in the solid compound K₃CoF₆¹⁶ the absorption band is observed at 13000 cm⁻¹, which is close to the band A in Fig. 1 occurring at 14000 cm⁻¹. The high value of the wave number for the absorption peak A (14000 cm⁻¹) as compared to the band at 13000 cm⁻¹ in K₃CoF₆ may be attributed to the polarisation of the ligands¹⁷, the relative positions of the oxygen and fluorine in the spectrochemical series and the inter-atomic separation between the ligands and the central metal ion. The band A could be attributed to the transition 5T_{2g} to 5E_g¹⁶. The value 14600 cm⁻¹, therefore, directly gives the crystal field splitting Δ for the high spin Co³⁺ ion in the spinel.

The absorption bands occurring at B (17240 cm⁻¹) and C (21275 cm⁻¹) in Fig. 1 may be due to the octahedrally surrounded Cr³⁺ ion in the spinel as the bands B and C are close to the positions of the bands at 16200 cm⁻¹ and 21600 cm⁻¹ observed for the octahedral Cr³⁺ ion in Cr₂O₃¹⁵ respectively. These bands (B and C) appear to occur due to the transitions 4A₂ → 4T₂ and 4A₂ → 4T₁ respectively¹⁶. The approximate value of the crystal field splitting for the Cr³⁺ ion in the spinel will be 17000 cm⁻¹ i.e., the position of the first band¹⁶. The difference between the values of the wave numbers of the two absorption bands B and C, and that observed in the case of Cr₂O₃ may be due to (1) the nature of the octahedral surroundings¹⁸, (2) the surroundings in the first and higher coordination spheres and (3) probable cation-cation interaction in the two systems.

In case of thin layers of ZnO, Weiss¹⁹ has observed the peak at 3.3 V (27000 cm⁻¹) in the absorption spectrum. The absorption peak D occurring at 28570 cm⁻¹ must then be due to Zn²⁺ ion. This peak can be explained on the basis of the M.O. theory. The qualitative M.O. diagrams for a tetrahedral chromium CrO₄²⁻ ion have been employed by Viste and Gray²⁰ and Fischer¹⁸ for explaining the features of the optical spectrum of CrO₄²⁻ ion. It is possible to

extend the use of these M.O. pictures to the post-transition metal tetrahedral ion like SbO₄³⁻, where penta-valent Sb⁵⁺ possesses 4d¹⁰ electron configuration²¹. The electron configuration for Zn²⁺ ions is also 3d¹⁰. The M.O. picture given by Viste and Gray²⁰ and Fischer¹⁸ can thus be used for interpreting the band D. The qualitative M.O. diagram for Zn²⁺ tetrahedral ions is shown in Fig. 2 (a and b). The band D

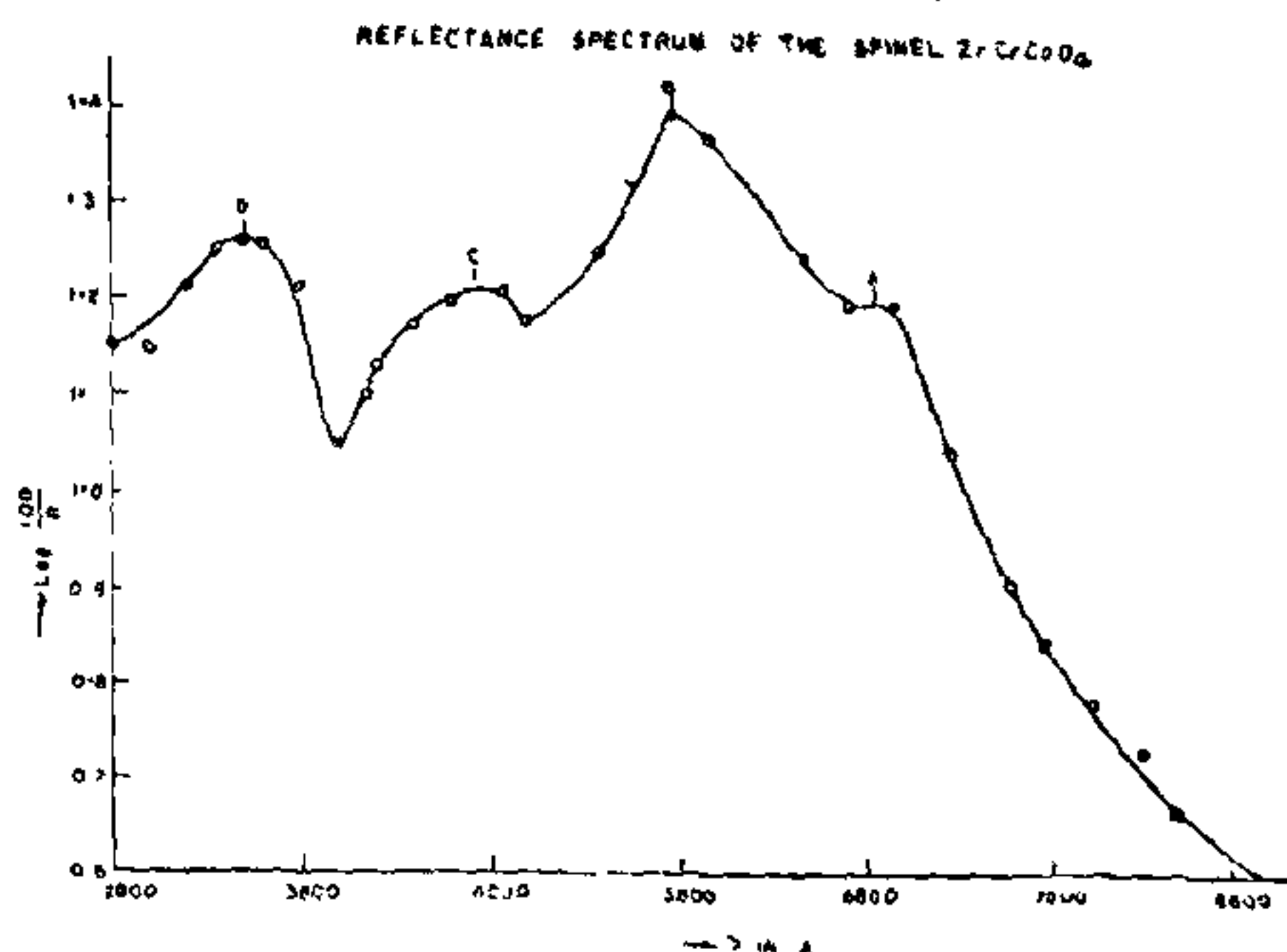


FIG. 1

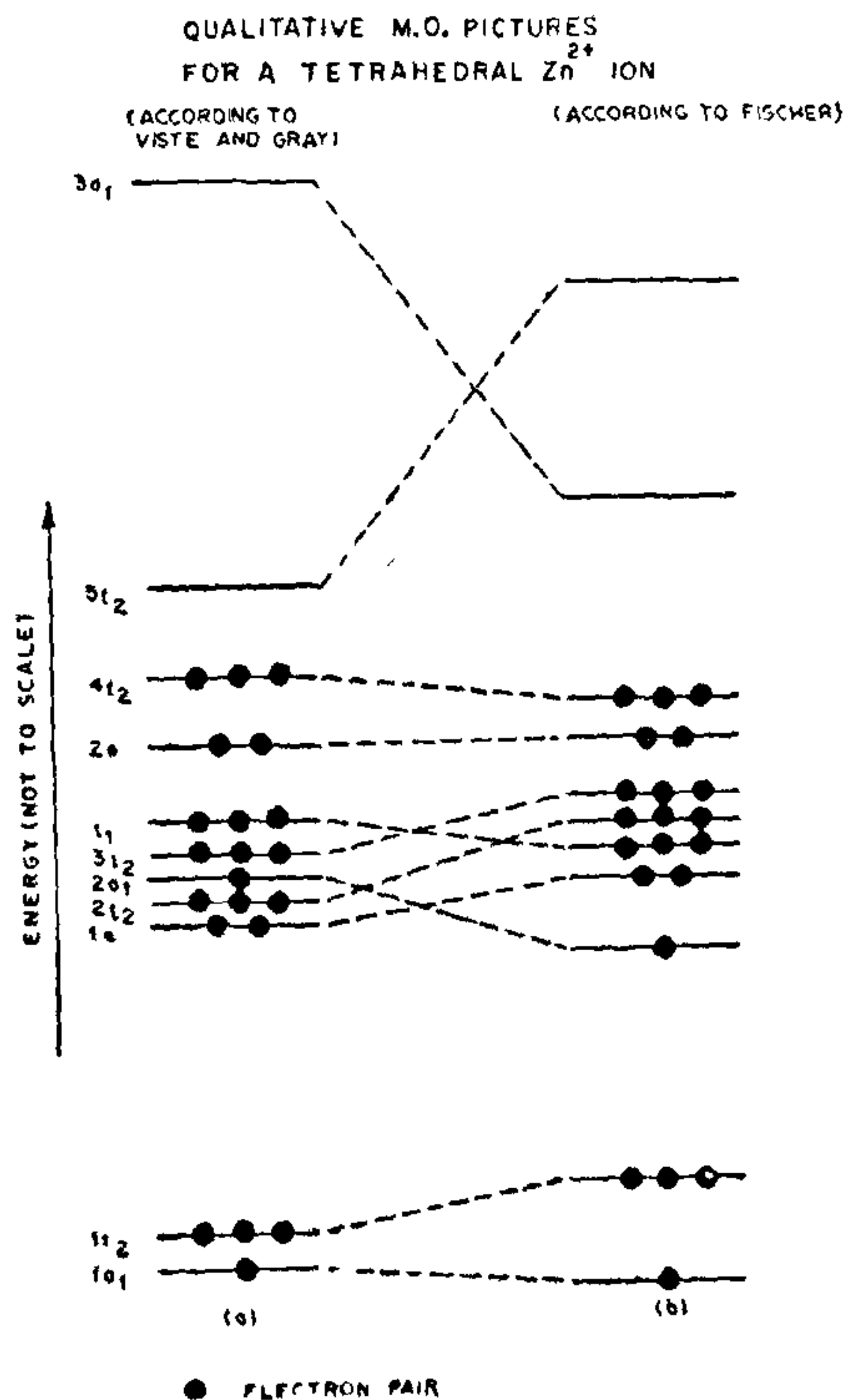


FIG. 2

at 23570 cm^{-1} could be assigned to the transition of electrons from $4t_2$ to the next empty $5t_2$ level [Fig. 2(a)] or from $4t_2$ to $3a_1$ level [Fig. 2(b)].

It is worthwhile to mention²¹ that in the case of post-transition metals (Cu^+ , Ag^+) the absorption bands are attributed to transitions between the two states d^{10} and d^9s . In this context the assignment $4t_2$ to $3a_1$ seems to be more appropriate.

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1. Kshirsagar, S. T. and Biswas, A. B., *Physics Chem. Solids*, 1967, **28**, 1493.
2. Kulkarni, D. K. and Mande, C., *Acta Crystallogr.*, 1971, **B27**, 2044.
3. — and —, *Indian J. Pure Appl. Phys.*, 1974, **12**, 60.
4. Rossiter, M. J., *Physics Lett.*, 1966, **21**, 128.
5. Yagnik, C. M., *Ph.D. Thesis*, Poona University, Poona, 1967.
6. Verway, E. J. W. and Heilman, R. L., *J. Chem. Phys.*, 1947, **15**, 174.
7. Kshirsagar, S. R., *J. Phys. Soc. Japan*, 1969, **27**, 1164.
8. Borgers, P. F., *Ph.D. Thesis*, Leiden University, Leiden, 1957.
9. Szymczak, H., Wardzynska, M. and Mylnikova, I. E., *J. Physics (c)*, 1975, **8** (22), 3937.
10. Wood, D. L., Imbusch, G. E., Macfarlane, R. M., Kisliuk, P. and Larlain, D. M., *J. Chem. Phys.*, 1968, **48**, 5255.
11. Kahan, H. M. and Macfarlane, R. M., *Ibid.*, 1971, **54**, 5197.
12. Mande, C. and Chetal, A. R., *Rontgenspectren and Chemische Bindung*, Leipzig, Physikalisch, Chemisches Institut der Karl Marx Universität, 1965.
13. Henry, N. F. M., Lipson, H. and Wooster, W. A., *The Interpretation of X-ray Diffraction Photographs*, Macmillan, London, 1961.
14. Orgel, L. E., *An Introduction to Transition Metal Chemistry*, Methuen and Co. Ltd., London, 1960.
15. Jorgenson, C. K., *Absorption Spectra and Chemical Binding in Complexes*, Pergamon Press, New York, 1962, pp. 170, 293, 290.
16. Figgis, B. N., *Introduction to Ligand Fields*, Wiley, New York, pp. 222, 229.
17. Ferguson, J., Knox, K. and Wood, D. L., *J. Chem. Phys.*, 1951, **35**, 2236.
18. Fischer, D. W., *Int. Conf. on Band Structure Spectroscopy of Metals and Alloys*, Univ. of Strathelyde, Glasgow, Scotland, 1971, p. 19 and Fig. 11.
19. Weiss, H., *Z. Phys.*, 1952, **132**, 335.
20. Viste, A. and Gray, H. B., *Inorg. Chem.*, 1964, **3**, 1113.
21. McClure, D. S., *Electronic Spectra of Molecules and Ions in Crystals*, Academic Press, New York, 1959, pp. 171, 174.

ROLE OF PROTEIN BACKBONE IN SPECIFIC RECOGNITION OF NUCLEIC ACID BASE SEQUENCES: A HYPOTHESIS

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ABSTRACT

A novel H-bonding scheme of interaction between protein backbone and nucleic acid base pairs has been proposed. The importance of such an interaction in specific recognition of base sequences in double helical nucleic acids has been discussed. It is concluded that protein backbone can play very important role in specific recognition of base sequences.

1. INTRODUCTION

THE specific recognition of nucleic acid base sequences by proteins is a fundamental process at several steps of genetic expression. Several attempts have been made¹⁻¹² to understand this key phenomenon. It has been suggested that proteins can interact with nucleic acids in four different ways¹, viz., via electrostatic interaction, stacking, hydrogen bonding and hydrophobic interaction. Among these, hydrogen

bonding interaction between amino acid residues and nucleic acid bases is, by far, the most efficient process in the specific recognition of nucleic acid bases, because of the directional nature of the H-bond. Several H-bonding schemes have been suggested and these are centered on specific interactions between amino acid side chains and bases in DNA. It has been suggested that at least two H-bonds are needed for specific recognition of a base pair³. In this communication we propose a new scheme of H-bonding interaction