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Multiple-scattering resonances and structural effects in the x-ray-absorption near-edge spectra of Fe II and Fe III hexacyanide complexes

A. Bianconi and M. Dell'Ariccia
Istituto di Fisica, Università di Roma, I-00185 Roma, Italy

P. J. Durham and J. B. Pendry*
Science and Engineering Research Council, Daresbury Laboratory,
Daresbury, Warrington WA4 4AD, United Kingdom

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The x-ray-absorption near-edge structure (XANES) at the Fe*K* edge of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ has been measured and interpreted by means of multiple-scattering calculations. The theory is able to account for the XANES over a 40-eV energy range. We demonstrate that the quasidiatomic "shape resonances" arising from multiple scattering within the CN groups play an important role in the XANES and suggest that this may be a common feature of XANES of metal atoms bound to molecular groups (e.g., CO, CN, ...) containing multiple bonds. The effects on the XANES of bond-length changes and distortions of the coordination geometry of the $Fe(CN)_6$ cluster have been estimated. The different XANES spectra of $[Fe(CN)_6]^{2+}$ and of $[Fe(CN)_6]^{3+}$ have been interpreted in terms of charge-induced structural modifications. Comparison of XANES with extended x-ray-absorption fine-structure (EXAFS) and diffraction data shows that XANES can be used as a quantitative probe of local structure distortions which are not detected by EXAFS.

I. INTRODUCTION

Interest in local structure determination for complex systems like proteins, surfaces, and amorphous materials has renewed attention on the x-ray-absorption near-edge structure (XANES).[1,2] In fact, from XANES it is possible to obtain complementary information to that extracted from extended x-ray-absorption fine structure (EXAFS) concerning the coordination geometry and the effective charge on the absorbing atom, and so this is particularly important in the study of systems for which EXAFS is of limited usefulness.[3]

Although x-ray-absorption spectra were measured for many years using standard x-ray sources, only a qualitative interpretation of XANES was attempted, and experiments were limited to simple systems. Recently a multiple-scattering approach to the calculation of XANES has been proposed,[2] and the use of synchrotron radiation makes feasible experiments on XANES of very dilute complex systems like proteins and surfaces.[1]

In this paper, we report a quantitative interpretation of the XANES of Fe II and Fe III hexacyanide complexes. Interest in ferro- and ferri-hexacyanide complexes has been recently aroused on account of their analogies with the iron-heme system in proteins like hemoglobin (Ref. 4) and cytochrome C. In fact, in these systems Fe takes part in appreciable delocalized π bonding, and the charge distributions and the related structural differences between different charge states of these complexes are difficult to determine. In fact, in hemoglobin[4] and cytochrome C (Ref. 5) little or no contraction, respectively, of the Fe-N distance has been found in reduction processes from EXAFS studies. This effect has been interpreted as evidence of the electronic "back-donation" effect first predicted in iron hexacyanides.[6]

The XANES of transition-metal atoms bound to CN or CO groups are dominated by sharp and strong peaks,[7–10] characteristic features which have not yet been fully understood. This class of ligands is characterized by a short interatomic distance typical of multiple bonds. Prototypes of these systems are $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, which contain a stable octahedral $Fe(CN)_6$ complex for two formal charge states of the Fe atom [Fe II and Fe III, respectively].

We have measured the XANES and EXAFS of these systems using synchrotron radiation, and find that we can interpret the main features of the near edge using our multiple-scattering calculations. The results show that the XANES of these systems are related to the "shape resonances" of the CN groups, in which the excited electron in the continuum is virtually "trapped" (i.e., strongly multiple scattered) within the CN groups. Our analysis shows that XANES is sensitive to the C-N distance, and this seems to be a promising approach to the determination of small variations for the C-N or C-O distances. Moreover, the effect on XANES of distortions of the octahedral coordination geometry up to the second coordination shell have been estimated.

We have found the same average Fe-C distance in the two charge states of $Fe(CN)_6$ complex from EXAFS data analysis, but the analysis of the XANES spectra shows the presence of subtle charge-induced distortions of the symmetry, together with variations of the C-N distances.

II. EXPERIMENT

The experiments were made at the synchrotron radiation facility Progetto per l'Utilizzazione della Luce di Sincrotrone (PULS) in the Frascati Laboratories. Synchrotron radiation emitted by the ADONE storage ring, working at 1.5 GeV and 30 mA, was monochromatized by a Si(220) channel-cut single crystal at 17 m from the source. The energy resolution at $\hbar\omega = 7$ keV was $\Delta E/E = 10^{-4}$. The absorption was obtained from transmission data. The samples were in the form of powder layered between two thin sheets transparent to x rays.

III. RESULTS AND DISCUSSION

Figure 1 shows the XANES and EXAFS at the FeK edge of the Fe II and Fe III complexes. The pre-edge continuum background has been subtracted by fitting the pre-edge part of the spectra. The high-energy smooth atomic absorption α_A, due to core transitions from the 1s core level to continuum p states for the single Fe atoms, has been obtained by fitting the high-energy part of the spectra (the EXAFS region above 7190 eV) by a polynomial. The calculated relative absorption over the EXAFS and XANES regions with respect to α_A, i.e.,

$$(\alpha_M - \alpha_A)/\alpha_A ,$$

where α_M is the measured absorption, is plotted in Fig. 1. This procedure allows the normalization of different spectra to the continuum atomic absorption α_A, which is expected to be the same for all spectra of the same absorbing atom.

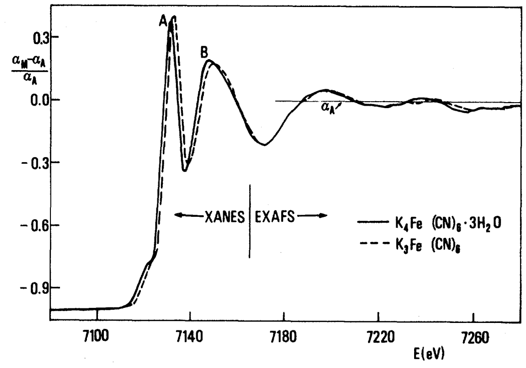

FIG. 1. X-ray-absorption spectra of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The XANES and EXAFS are plotted in the same figure. The relative absorption with respect to the high-energy continuum atomic background α_A is plotted.

The data show that the XANES is dominated by two strong and sharp peaks A and B (relative absorption maxima ~40%) and the EXAFS by weak oscillations (relative absorption maxima ~5%).

It is clear from the spectra that the EXAFS parts of the two spectra are very similar, while the main differences appear in the XANES region. The XANES are different with regard to the energy, intensity, and shape of peaks A and B.

A. Interatomic distances from EXAFS and diffraction

An EXAFS analysis has been carried out, and the Fourier transform over a limited wave vector k range between 4 and 8 Å^{-1} is plotted in Fig. 2. The two peaks of the Fourier transform, which gives the atomic pair correlation function, correspond to the C and N near neighbors. The Fe-C distances are very close in the two systems. The analysis of the phase differences between the Fourier anti-

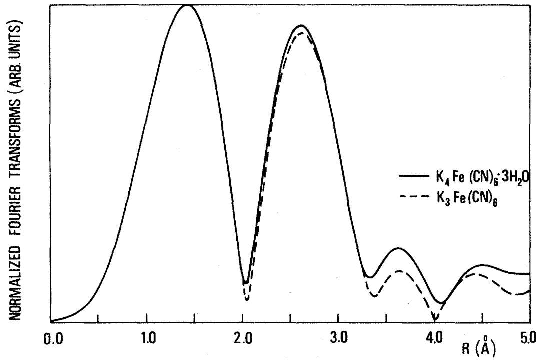

FIG. 2. Fourier transforms of the EXAFS oscillations between 4 and 8 Å^{-1}.

transforms of only the first C coordination shell of the two systems was used to determine the variation of the Fe-C distance.[1] We have not been able to identify a variation of this distance between the two complexes larger than 0.01 Å. Taking account of the limited wave vector k range and systematic errors in EXAFS data analysis, we estimate that the *average* Fe-C distance measured[3] by EXAFS is the same in the two systems within ±0.02 Å. This result is in agreement with the EXAFS experiment of Eisenberger and Lengeler,[3] but it is in disagreement with the results reported by Tolkiehn *et al.*[11] who give a longer Fe-C distance in $[Fe(CN)_6]^{3+}$ by 0.03 Å.

Neutron diffraction experiments by Taylor *et al.*[12] on $[Fe(CN)_6]^{2+}$ and x-ray-diffraction experiments by Figgis *et al.*[13] on $[Fe(CN)_6]^{3+}$ give a contraction of the average Fe-C distance by 0.026 Å in the Fe III complex going from 1.929 to 1.903 Å. Taking account of the effect of distortions observed in diffraction data, our EXAFS data are not inconsistent with these experiments. On the contrary, we are in disagreement with the large average Fe-C distance for $[Fe(CN)_6]^{2+}$ reported by Kiriyama *et al.*[14]

The diffraction experiments[12,13] give a contraction of the average C-N distance from 1.161 to 1.133 Å in the Fe II and Fe III complexes, respectively. To measure this contraction from EXAFS data, one should determine the Fe-N distance, but the C atoms shadow the N atoms in the second shell. This effect introduces large multiple-scattering effects to the EXAFS oscillations, which can no longer be explained by the standard single-scattering theory. This "focusing effect" produces the anomalously large intensity of the nitrogen peak in the Fourier transform in Fig. 2 and a phase shift on the oscillations.

B. XANES theory

We have investigated the near-edge structure with the help of a multiple-scattering theory of XANES recently developed by Durham, Pendry, and Hodges.[2] This method uses a muffin-tin form for the potential of each atom and gives good results for close-packed solids.[15] For the more molecular materials under consideration here, the muffin-tin approximation is not good, but although we regard our results as somewhat qualitative, the calculations do shed light on the nature of the near-edge structure. We constructed our potentials according to the Mattheiss prescription common in band-structure calculations[16] by overlapping neutral-atom charge densities and spherically averaging the resulting potential within each muffin-tin sphere. This is clearly a crude representation of the true potential function, and in particular makes no serious attempt to model the actual charge distribution. The self-consistent-field $X\alpha$ calculations of Kutzler *et al.*[17] may give a better idea of this distribution, but they also make use of the muffin-tin approximation. Our main aim was to examine the effect on the XANES of changes in the bond geometry alone, and our potentials are probably adequate for this purpose.

Figure 3 shows the calculated XANES for several bond lengths. In the upper panel [Fig. 3(a)], the Fe-C distance is varied with the C-N distance held constant. It can be seen that the two major features, peaks A and B, are clearly reproduced, showing that our estimate of the scattering power of each atom is not, in fact, unreasonable. The effect of changes in the Fe-C distances is to produce an essentially uniform shift of the structures.

The lower panel, Fig. 3(b), shows the effects of varying the C-N distance for a fixed Fe-C distance.

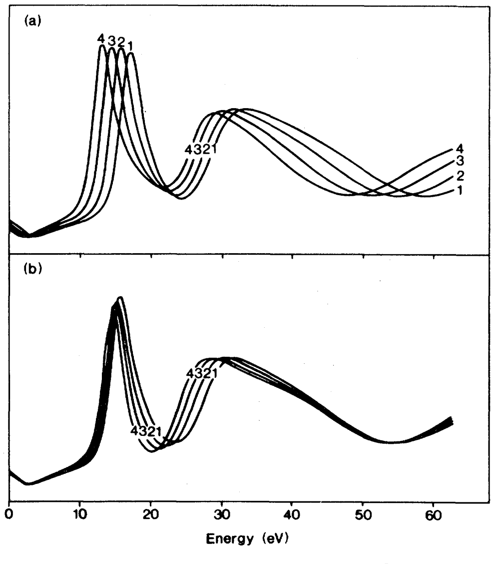

FIG. 3. Calculated K-edge XANES of $Fe(CN)_6$ clusters: (a) C-N distance fixed at 1.134 Å, Fe-C distances of 1.852 Å (curve 1), 1.903 Å (curve 2), 1.958 Å (curve 3), and 2.011 Å (curve 4). (b) Fe-C distance fixed at 1.903 Å, C-N distances of 1.134 Å (curve 1), 1.164 Å (curve 2), 1.191 Å (curve 3), and 1.217 Å (curve 4). (The zero of energy in Figs. 3, 4, and 6 is chosen to be close to the d resonance on the Fe atom. It does not represent an accurate determination of the threshold but should be quite close to it.)

Now the splitting between peaks A and B also changes, as well as their relative intensity. This sensitivity to the C-N distance is an indication of the importance of the "shape resonance" within the CN group. In fact, the internal photoelectron initially excited at the Fe site can, owing to strong multiple scattering within the CN groups, be trapped in quasibound resonant states in the continuum. It is well known that the energy splitting between two classical shape resonances (π_g and σ_u) in diatomic molecules varies strongly with the bond length.[18] This suggestion is reinforced by Fig. 4, which shows a calculation for a hypothetical FeC_6 cluster, i.e., $Fe(CN)_6$ with the N atoms removed. Clearly, the strong multiple scattering between the C and N atoms plays an important role in the XANES of $Fe(CN)_6$ complexes.

C. Differences between the XANES of Fe II and Fe III complexes

The observed variation of the XANES going from the Fe II to the Fe III complexes can be investigated by considering the effect of small structural variations on the calculated XANES. Figure 5(b) shows in detail the XANES of the two compounds, together with the derivative spectra. The weak structures labeled 1–3, at the absorption threshold, within an 8-eV energy range, are due to final unoccupied valence states.[10] This energy range can be called the "edge region" and can be explained by molecular-orbital theory, which has been applied for many years to interpretation of the edge spectra. Following this approach, the features should be assigned to the unoccupied valence states $3e_g$, $4t_{1u}$, $2t_{1g}$, and $5t_{1u}$ calculated by Alexander and Gray.[19] The feature labeled 3 lies in an energy range where, in most of the K spectra of transition-metal compounds,[18,20] there is the rising threshold of the $1s \rightarrow \epsilon p$ dipole-allowed transitions. In the spectra in Fig. 5(b), the intensity of this feature is weak in comparison with spectra of other systems. This effect is probably due to the transfer of the oscillator strength from the continuum to the strong multiple-scattering resonances A and B.

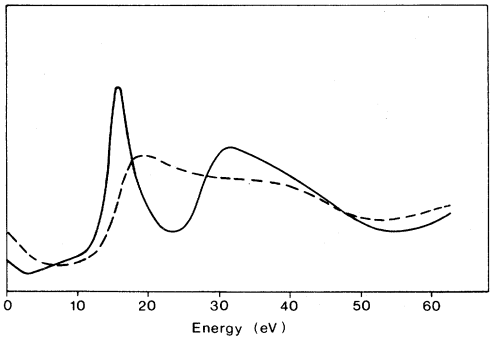

FIG. 4. Calculated XANES for a $Fe(CN)_6$ cluster ($R_{Fe\text{-}C} = 1.903$ Å, $R_{C\text{-}N} = 1.134$ Å) with both C and N shells included (solid curve) and with the C shell only included (dashed curve).

The resonances A, B, and C in the continuum part of the absorption spectrum dominate the "XANES region." The strong resonances A and B, as well as the shoulder C, are well predicted by our calculations shown in Fig. 3. A detailed analysis of

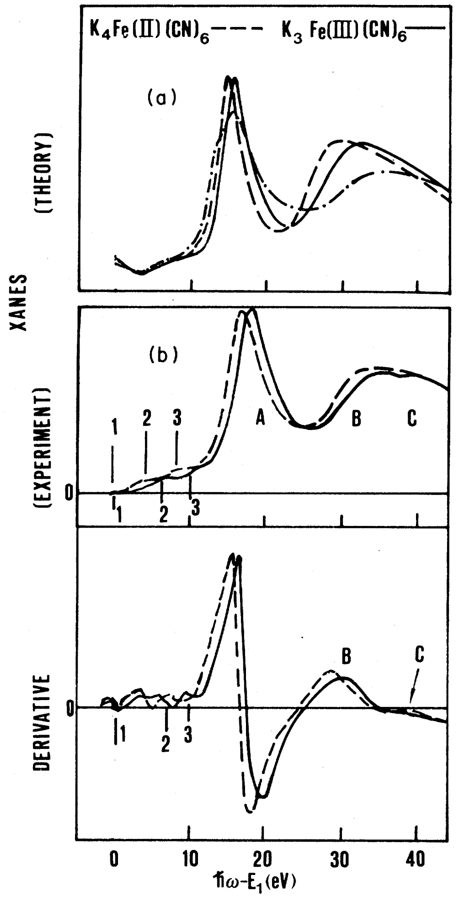

FIG. 5(a) Calculated XANES of $[Fe(CN)_6]^{2+}$ and $[Fe(CN)_6]^{3+}$ using the diffraction data. The solid line is obtained using the coordinates of Figgis *et al.* (Ref. 13) for $[Fe(CN)_6]^{3+}$. The dashed line is the XANES of $[Fe(CN)_6]^{2+}$ using the coordinates given by Taylor *et al.* (Ref. 12). The dashed-dotted line is the XANES spectrum using the coordinates of $[Fe(CN)_6]^{2+}$ reported by Kiriyama *et al.* (Ref. 14). (b) XANES (upper panel) and the derivatives (lower panel) for the Fe II and Fe III complexes. The zero of the energy scale is taken at the absorption maximum of the first feature, 1, of the Fe II complex. This feature shifts by 0.5 eV in the Fe III complex.

the resonances *A*, *B*, and *C* in the two spectra shows important differences. Peak *A* is shifted by 1±0.2 eV but its line shape remains the same within the experimental noise. Peak *B* also shifts toward higher energy in the Fe III spectrum, but its line shape is quite different in the two spectra. In the Fe II spectrum its rising edge is quite sharp, while in the Fe III it is much broader and, normalizing the spectra at the intensity of peak *A*, it is weaker. Also, the shape of the spectra in the region of the shoulder *C* is different. The structure *C* is much clearer in the Fe III complex.

D. The chemical shift of peak *A*

The shift of peak *A* by 1±0.2 eV going from Fe II to Fe III complex can be associated with (1) a different binding energy of the 1*s* core initial state, (2) different Fe-C distances, or (3) different C-N distances.

The x-ray photoelectron spectroscopy gives a chemical shift of the 2*p* core level of about 1 eV.[21] Assuming a similar chemical shift for the 1*s* core level, the chemical shift of peak *A* could be entirely assigned to a shift of the initial-state binding energy. In this case the final states of the transition *A* are at the same energy position in continuum in both spectra, and the results in Fig. 3 would then imply that the Fe-C distance should be the same in both the Fe II and Fe III complexes.

We discuss now the second possible explanation of the shift of peak *A*. If we assume that all the shift of peak *A* is due to a shift of the multiple-scattering resonances, Fig. 3(a) indicates that this effect could be due to a contraction of the Fe-C distance in the Fe III complex by 0.04 Å. This is an upper value to the possible contraction because the shift can also be partially due to an initial-state shift. This result would be in agreement with the diffraction data[12,13] giving a 0.026-Å contraction and in disagreement with the EXAFS results of Tolkiehn *et al.* which show an expansion of 0.03 Å.[11]

The third possible effect which could induce a chemical shift of peak *A* is a variation of the C-N distance, but an unphysically large change of this distance is necessary to account for a 1-eV energy shift, as is shown in Fig. 3(b).

E. Energy separation between peaks *A* and *B*

The energy separations between peaks *A* and *B* are 16.5 and 17 eV in the Fe II and Fe III complexes, respectively. The increase of the energy separation by 0.5 eV between these peaks is likely to be due to a contraction of the C-N distance. A change either in the core-level binding energy, or in the Fe-C distance would, according to our calculations plotted in Fig. 3(a), induce a rigid energy shift of both peaks *A* and *B*. On the other hand, a contraction of the C-N distance induces an increase of the *A*-*B* separation. According to our calculations, a contraction of the C-N distance by about 0.02 Å in the Fe III complex can explain the observed effect. We regard this result as a qualitative result at this stage. However, this is in reasonable agreement with the diffraction data[12,13] which report a 0.028-Å contraction. Such a change in the C—N bond length would be likely if the extra charge in the Fe II complex were distributed over the CN groups, and this would also produce a 1*s* core-level shift, as discussed above. A more quantitative determination of the C-N distance is under way, including the effect of the charge distribution on the XANES.

F. Effect of distortions from octahedral symmetry

None of the simple explanations of the shift of peak *A* can account for the different line shapes of features *B* and *C* in the two complexes. To explain this difference it is necessary to include small distortions of the octahedral $Fe(CN)_6$ group. In fact, diffraction data show[12–14] that small distortions can be present, and that they are different in the two charge states of $Fe(CN)_6$. In Fig. 5(a) we show the results of calculations of XANES using the atomic coordinates given by the diffraction data. We find that using the data of Taylor[12] and Figgis[13] (see Table I), the calculated XANES agree with experiment. The shift of peak *A*, the broadening of *B*, and the stronger shoulder *C* appear in the XANES of the Fe III complex in comparison with that of the Fe II.

The calculated XANES of $[Fe(CN)_6]^{2+}$ with the use of the data of Kiriyama *et al.*[14] are in disagreement with the experiment. The large tetragonal distortion of the first coordination shell reported by these authors induces a distinct splitting of peak *A* which is not observed in XANES of $[Fe(CN)_6]^{2+}$.

Thus we find that the XANES of $[Fe(CN)_6]^{2+}$ and $[Fe(CN)_6]^{3+}$ are quite consistent with the diffraction data of Refs. 12 and 13, according to which the $[Fe(CN)_6]^{3+}$ has nearly octahedral symmetry, while $[Fe(CN)_6]^{2+}$ shows the presence of a small tetragonal distortion [the Fe-C distance is 0.04 Å longer in one direction (5-2), and the C-N distance 0.02 Å shorter than the corresponding average distances on the perpendicular plane].

TABLE I. Data of Taylor and Figgis to show that the calculated XANES agree with experiment.

	$K_3Fe(CN)_6$			$K_4Fe(CN)_6$	
	Figgis *et al.* (Ref. 13)			Taylor *et al.* (Ref. 12)	
	d (Fe-C) (Å)	*d* (C-N) (Å)		*d* (Fe-C) (Å)	*d* (C-N) (Å)
(4-1)	1.92	1.08	(1)	1.908	1.184
(5-2)	1.90	1.18	(4)	1.915	1.187
(6-3)	1.89	1.14	(5-2)	1.956	1.147
			(6-3)	1.920	1.150
Average	1.903	1.133		1.929	1.1608

IV. CONCLUSIONS

We have shown that the main multiple-scattering resonances in the XANES of $Fe(CN)_6$ complexes are associated with shape resonances within the CN ligands, the energy separation of peaks *A* and *B* and their dependence on the C-N distance being essentially as expected for the shape resonance of a CN group. An excited photoelectron of low kinetic energy (10–30 eV) emitted by the central Fe atom can be "trapped" in virtual bound states built up of repeated scatterings from the C and N atoms of a CN group. As a result, there is a resonant enhancement at these energies of the back-scattering amplitude of the ligand shell as a whole, and this is reflected in the absorption cross section in a way which depends on the geometrical arrangement of the CN groups around the Fe atom.

While EXAFS does not yield structural differences between the different charge states of the iron-hexacyanides, XANES indicates a distortion of the octahedral geometry as well as bond-length changes. The results are consistent with the idea of "back donation" of metal electrons to ligands.[6] According to this idea the effective charge on the Fe ion is the same in both compounds. Going from Fe III to Fe II complexes, the extra electron goes from the metal ion to the CN orbitals, and this probably gives rise to the contraction of the average C-N distance of 0.034 Å going from Fe II to Fe III charge states. However, this study shows that the charge of the extra electron in $[Fe(CN)_6]^{2+}$ may not be uniformly distributed over all the CN groups.

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[*] Present address: Department of Physics, Imperial College, London, UK.

[1] A. Bianconi, Appl. Surf. Sci. 6, 392 (1980).

[2] P. J. Durham, J. B. Pendry, and C. R. Hodges, Solid State Commun. 38, 159 (1981); Comput. Phys. Commun. (in press).

[3] P. Eisenberger and B. Lengeler, Phys. Rev. B 22, 3551 (1980).

[4] P. Eisenberger, R. G. Shulman, B. M. Kincaid, G. S. Brown, and S. Ogawa, Nature (London) 274, 30 (1978).

[5] C. Yuen, M. Weissbluth, and A. M. Labhardt, SSRP Report No. 77/06, Stanford University (unpublished).

[6] R. G. Shulman and S. Sugano, J. Chem. Phys. 42, 39 (1965).

[7] A. Cotton and G. P. Hanson, J. Chem. Phys. 26, 1758 (1957).

[8] W. Seka and H. P. Hanson, J. Chem. Phys. 50, 344 (1969).

[9] R. C. Shulman, Y. Yafet, P. Eisenberger, and W. E. Blumberg, Proc. Natl. Acad. Sci. U.S.A. 73, 1384 (1976).

[10] M. Obashi, Jpn. J. Appl. Phys. 17, 563 (1978).

[11] G. Tolkiehn, P. Rabe, and A. Werner, Daresbury Laboratory Report No. DL/SCI/R17 (Experimental) (unpublished).

[12] J. C. Taylor, M. H. Mueller, and R. L. Hitterman, Acta Crystallogr. Sect. A 26, 559 (1970).

[13] B. N. Figgis, M. Gerloch, and R. Mason, Proc. R. Soc. London Ser. A 309, 91 (1969).

[14] R. Kiriyama, H. Kiriyama, T. Wada, N. Niizeki, and

H. Hirabayashi, J. Phys. Soc. Jpn. 19, 540 (1964).

[15] G. N. Greaves, P. J. Durham, G. Diakun, and P. Quinn, Nature (London) 294, 139 (1981).

[16] L. Mattheis, Phys. Rev. A 134, 970 (1974).

[17] F. W. Kutzler, C. R. Natoli, D. K. Misemer, S. Doniach, and K. O. Hodgson, J. Chem. Phys. 73, 3274 (1980).

[18] A. Bianconi, in *EXAFS for Inorganic Systems,* edited by C. Garner and S. Hesnein (1981), p. 13; J. L. Dehmer and D. Dill, J. Chem. Phys. 65, 5327 (1976).

[19] J. J. Alexander and H. B. Gray, Coord. Chem. Rev. 2, 29 (1967).

[20] M. Belli, A. Scafati, A. Bianconi, S. Mobilio, L. Palladino, A. Reale, and E. Burattini, Solid State Commun. 35, 355 (1980).

[21] M. V. Zeller and R. G. Hayes, J. Am. Chem. Soc. 95, 3855 (1973).