PHYSICAL REVIEW B VOLUME 21, NUMBER 6 15 MARCH 1980

Nature of the $5f$ electrons in uranium nitride: A photoelectron spectroscopic study of UN, U, UO_2, ThN, and Th

P. R. Norton, R. L. Tapping, D. K. Creber, and W. J. L. Buyers

Atomic Energy of Canada Limited Research Company, Chalk River Nuclear Laboratories, Chalk River, Ontario KOJ 1JO, Canada

(Received 31 July 1979)

Ultraviolet and x-ray-photoelectron spectra of core and valence levels in U metal, UN, UO_2, Th, and ThN have been obtained. These spectra demonstrate the existence in uranium nitride of a sharp band of f states (containing 2.2 ± 0.5 electrons) at the Fermi level. The anomalously broad $4f$ core levels in UN are discussed in terms of several possible energy-loss mechanisms, including configuration interaction and alternating valency. No change is seen in the density of f states of UN on cooling through the antiferromagnetic transition.

I. INTRODUCTION

The actinide compounds exhibit a fascinating and often enigmatic array of magnetic and electronic properties.[1,2] To a large extent this is because the character of the $5f$ electrons is believed to be intermediate between the highly localized $4f$ electrons of the lanthanides and the strongly itinerant d electrons of the transition metals. Uranium nitride is a particularly good example of the competition between localization and itineracy since it has the smallest lattice constant (0.4885 nm) of the uranium pnictide series. Thus, although UN is antiferromagnetic below ~50 K, the Hill plot[3] shows that it is close to the boundary between magnetic and nonmagnetic behavior. The paramagnetic susceptibility[4] is consistent with an apparent moment of ~2.5 μ_B, yet the ordered moment[5] (the lowest of the uranium pnictides) is only 0.75 μ_B. This paradoxical behavior may be more apparent than real, for the extraction of a value for the paramagnetic moment implies the assumption of a localized model for the magnetic electrons. Very recent calculations[6,7] on UN have indicated that f states are present in the conduction band and that it contains between ~1.8 and 3 electrons. For USb, however, a configuration of $5f^3$ has been inferred from measurements of the anisotropy of the magnetic form factor.[8] Fewer f electrons might indeed be expected for UN with its much smaller lattice constant. The Zachariasen radii[9] suggest that in uranium nitride where $U-U=0.345$ nm the configuration is intermediate between f^2 ($U-U=0.354$ nm) and f^1 ($U-U=0.326$ nm).

In an attempt to elucidate the nature of the $5f$ electrons in actinide compounds, we report in this paper a detailed photoemission study of Th, ThN, U, UN, and UO_2. The measurements provide convincing evidence that the $5f$ electrons of UN are located in a narrow band cut by the Fermi energy. The resultant competition between itinerant and localized $5f$ behavior gives a partial explanation of the weak moment and unusual spin-wave response of uranium nitride.

II. EXPERIMENTAL

The measurements were made with a Vacuum Generator ESCA-3 photoelectron spectrometer[10] and the spectra reported here were typically acquired at pressures $<10^{-8}$ Pa. The x-ray photoemission and ultraviolet (uv) photoemission spectra (XPS and UPS) were run at resolutions of ~1.2 and 0.15 eV, respectively. The samples could be heated to >1300 K and cooled to ~18 K.

A. UN, UO_2, and U metal

The uranium-nitride single crystal was cut by a diamond saw to expose a plane surface and then cleaned as outlined below. The present studies showed that the use of Xe^+ ions minimized any preferential sputtering of nitrogen relative to uranium. After pumping to $<10^{-8}$ Pa, the surface was sputtered with 5-keV Xe^+ ions to remove ~3–5 nm of oxide and carbon contamination. The stoichiometry of the surface was monitored by measuring the N $1s$/U $4f$ ratio (Al-$K\alpha$ excitation) after (a) sputtering, (b) sputtering followed by heating to 1200 K in vacuum which should favor the formation[11] of $UN_{1.0}$, (c)—(b) followed by heating to 1200 K in N_2 at 6×10^{-4} Pa, and (d) heating to 1200 K followed by addition of ~200-Pa N_2. The change in the stoichiometry over this range of treatments was <5% so the spectra shown below are representative of UN and not a nitrogen-depleted surface layer or a higher nitride.

Uranium oxide was grown from the clean UN surface by exposing it to ~10^{-1} to 1 Pa s of O_2 at room temperature. The XPS and UPS spectra obtained in this way were very similar to previously published[12] spectra of UO_2 and the oxide is therefore assumed to be stoichiometric.

Uranium-metal spectra were obtained from a disc of uranium that had been mechanically polished and then subjected to several hours of sputtering with 5-keV Ar^+ ions at current densities of ~10 $\mu A\ cm^{-2}$. It was essential to maintain the pressure $<10^{-8}$ Pa to prevent oxide growth. The spectra obtained after deliberate exposures to O_2 (~1 Pa s) were identical to those obtained by room-temperature oxidation of UN.

B. Th and ThN

To provide a measure of the non-*f* electronic density of states, spectra were also taken of thorium metal and thorium nitride. The ThN was prepared in *situ* from thorium metal (after cleaning by Xe^+-ion bombardment) by exposing the clean Th surface to ~200 Pa N_2 at 1200 K for a few seconds. The resulting nitride was examined for stoichiometry by measuring the N 1*s*/Th 4*f* ratio and scaling to UN by the calculated cross sections[13] and the known variation of sensitivity of the spectrometer with kinetic energy. On this basis, the stoichiometry of the thorium nitride was given by the formula ThN_{1-x} where $x < 0.1$, equal within experimental error to that of the UN sample.

III. RESULTS AND DISCUSSION

A. Valence-band spectra

The photoemission results for Th, ThN, U, UN, and UO_2 obtained with $h\nu = 40.8$-eV radiation are shown in Fig. 1. The Th and ThN spectra [Fig. 1(a)] were acquired under similar experimental conditions, so the relative intensities of these two spectra should be correct to ±20%. As shown in Fig. 1(a), the formation of ThN results in the complete removal of emission intensity within 1.3 eV of the Fermi level. Since in clean Th metal this emission must be from the 6d levels, the implication is that the *d* electrons are involved in chemical bonds in ThN. The weak structure at 6 eV in the Th-metal spectrum is due to the presence of a small amount of either an oxide or adsorbed oxygen (equivalent to ~5% of a monolayer from the XPS results). The structure at 9 eV is assigned to the Th 6*p* level ionized by He II β radiation (Th 6*p* binding energy $E_b = 16.6$ eV)[14] and the relative intensity of He II β: He II α is ~5%.

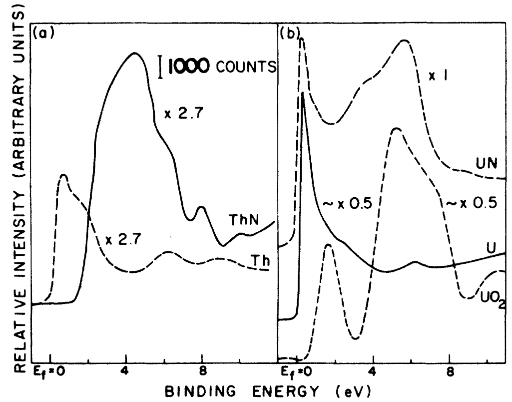

FIG. 1. Valence-band photoemission spectra ($h\nu = 40.8$ eV) of (a) Th metal and ThN; (b) U metal, UN, and UO_2. Numbers by spectra are factors by which spectra are magnified before display. Counting-statistic errors are of the order of magnitude of the thickness of the line drawn.

The valence-band spectra of U metal and UN are also shown in Fig. 1(b). The UN spectrum is very similar to that reported recently,[6] however, the U metal spectrum at 40.8 eV has not been published previously. An intense narrow peak [full width at half maximum (FWHM) ~1.5 eV] is observed at the Fermi level in the U and UN spectra which is not present in ThN [Fig. 1(a)]. Even in Th metal where the valence-band emission has moved up to E_f, the intensity is only one-tenth of the U emission at E_f.

The similarity of the bands in ThN and UN between 2 and 6 eV is shown in Fig. 1 and again in Fig. 2(a) at a higher photon energy ($h\nu = 1486.6$ eV). The relative sensitivities are preserved (to ±20% accuracy) in these spectra. The valence-band photoemission in ThN is mostly of Th 6*d*–N 2*p* character and thus it is argued that the structure in the UN spectrum between 2 and 6 eV is also largely of U 6*d*–N 2*p* character. This conclusion is supported by simple chemical bonding considerations as well as detailed theoretical calcula-

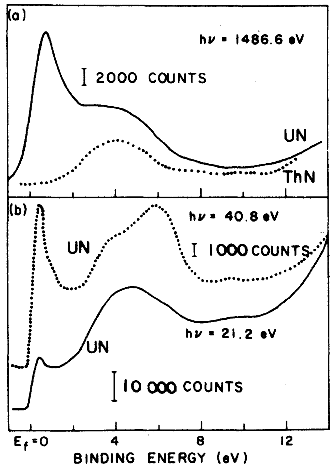

FIG. 2. Valence-band photoemission spectra of (a) UN and ThN at $h\nu = 1486.6$—Spectra acquired at same relative sensitivity; (b) UN at $h\nu = 21.2$ and 40.8 eV. Counting-statistic errors are of the order of magnitude of the thickness of the line drawn.

tions[6,15] although there is probably a contribution from *f*-*p* hybridization.[7] The observed bandwidth of this valence band (~4 to 5 eV) is also in good agreement with recent calculations.[7] As in ThN, it is therefore likely that in UN the 6*d* density is largely removed from the region close to E_f. The sharp peak at E_f in UN (but not necessarily in U where the bonding is different) is expected to be predominantly 5*f* in character.

Although the U and UN spectra were acquired on different samples with the concomitant changes in sample position, angle, roughness, etc., all of which could change the intensity of the spectra, it appears that the peak at the Fermi level in U is more intense at 40.8 eV than that observed in UN, probably because of the presence of U 6*d* electrons at the Fermi level in uranium metal. The emission at 1486.6 eV from UN shows no evidence for a sharp peak in the range 2–6 eV that might arise from the presence of 5*f* electrons in the valence band, as suggested for USb by Lander *et al.*[16]

Further evidence of the 5*f* character of the sharp peak in UN is provided by the dramatic growth in its intensity relative to the valence band between 2 and 6 eV as the photon energy increases from 21.2 to 1486.6 eV (Fig. 2), as expected for *f* electrons.[13,17] The spectrum of ThN obtained with Al-*Kα* radiation is also shown in Fig. 2(a) and illustrates the significant enhancement of emission intensity in UN compared to ThN. This intensity enhancement of *f* over *d* cross sections has also been seen by Fuggle *et al.*[14] in XPS studies of Th and U metals and further confirms that the peak in UN is largely of 5*f* character.

From the results at 1486.6 eV where the *f* cross section dominates, a calculation based upon the relative intensities of the 5*f* peak (Fig. 2) and the N 1*s* peak (Fig. 3) suggests, with the aid of Scofield's cross sections,[13] that in UN there are 2.2 ±0.5 electrons in the 5*f* band near E_f. There are of course large uncertainties in determining the background under the 5*f* peak. Calculations by Brooks and Glötzel[7] have indicated that there are 2.45 *f* electrons in UN, of which ~1.8 could reside in an *f* band near E_f, in fair agreement with our experimental observations.

In an attempt to assess the reliability of the present measurements of the number of *f* electrons in the 5*f* band near E_f, we have performed similar calculations on the photoemission data for Th metal. The calculation gave the reasonable result that there are 2.6 ±0.7 6*d* electrons in the thorium-metal conduction band.

The high density of states at the Fermi energy of UN observed at all photon energies, including the high-resolution uv spectra, shows the 5*f* electrons lie in a narrow band of FWHM ≳1 eV. A sharp *f* level at zero apparent binding energy is also observed in *α* uranium (Ref. 18 and Fig. 1) and ferromagnetic uranium sulphide.[6,17] Although we cannot exclude the possibility of large relaxation effects pinning the apparent position of the 5*f* level at E_f, a 5*f* level at E_f does emerge readily from recent cluster calculations for the actinide compounds.[6,19] Also, relaxation effects do not shift the apparent position of the 4*f* electrons in analogous lanthanide compounds from several eV below E_f to close to E_f (see Campagna and Wertheim[20] for a survey). Exceptions to this general behavior include SmS, TmTe, and CeN where intermediate valency is believed to exist. For example, the valence spectrum[21] of CeN is qualitatively similar to the spectrum of Un (Fig. 2). Baer and Zürcher[21] interpret the sharp peak at E_f in CeN as arising from the additional electron of Ce fluctuating between *f* and *d* symmetry. They place the *d* band 2–3 eV below E_f. Uranium nitride also conforms to one criterion for alternating valency in that the Fermi level cuts a narrow *f* band.[22]

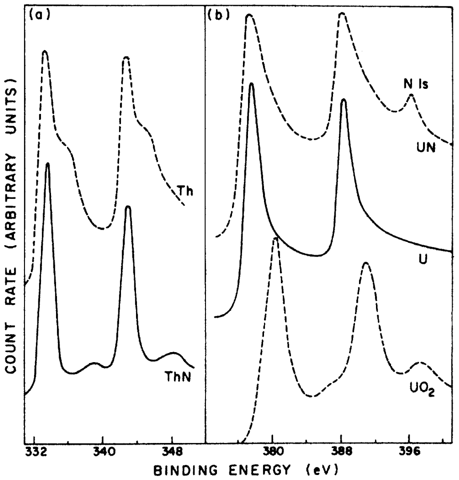

FIG. 3. 4*f* core-level photoemission spectra ($h\nu$ = 1486.6 eV) of (a) Th metal and ThN; (b) U metal, UN, and UO_2. Counting-statistic errors are smaller than the thickness of the line used to draw the spectra.

B. Core-level spectra

The 4*f* core levels in the present actinide compounds exhibit interesting structure and changes in linewidth that can be used to better characterize the valence bands. The 4*f* core-level spectra of Th metal, ThN, U metal, and UN ($h\nu$ = 1486.6 eV) are shown in Fig. 3. Also shown is the 4*f* core-level spectrum of UO_2 grown *in situ* from UN or U metal. uv-photoelectron spectra [shown in Fig. 1(b)] show that in UO_2 the U 5*f* band moves to ~1.5 eV below E_f. The U 4*f* levels are also stabilized in the oxide by 2.6 eV relative to UN.

By comparing the line shapes of the various compounds it is possible to draw some conclusions about the observation (Fig. 3) that the linewidth in UN is very large (4.6 eV FWHM) and asymmetric. This linewidth is ~2.5 times larger than in U metal (Fig. 3).

The Th 4*f* spectrum of Th metal shows a discrete loss at 2.5-eV higher-binding energy than the principal 4*f* peak. This structure has been previously reported by Fuggle and co-workers.[14] The shoulder can be attributed to a shake-up transition involving the Th 6*d* electrons. The itinerant character of the Th 6*d* electrons should prevent effective coupling with the 4*f* core hole so there is no possibility of multiplet splitting giving rise to this structure. In ThN the Th 6*d* level is stabilized relative to Th metal by ~4 eV (Fig. 1) and thus the energy of a shake-up transition from the Th 6*d* level is expected to increase by ~4 eV over that observed in Th metal. The intensity of the transition is also expected to decrease. This behavior is observed in ThN (Fig. 3) as a satellite peak at $\Delta E = 5.5$ eV. The satellite peak in ThO_2 at $\Delta E = 6.9$ eV has been assigned to this same type of shake-up transition.[23] Configuration interaction is expected to be very important in these compounds in which each shell has ~ twice the binding energy of the next least tightly bound shell.[24] The linewidth of the parent 4*f* lines in ThN is ~1.6 eV and they are quite symmetric. In this compound there is no appreciable density of states of E_f.

In contrast in U metal, which also exhibits intense and narrow (~1.7 eV FWHM) 4*f* core levels, the lines are quite asymmetric. In particular the tail on the high-binding-energy side appears to decrease exponentially with increasing binding energy. This appears to be an excellent example of the shake-up mechanism discussed by Wertheim and Citrin[25] in which the sudden occurrence of a core hole causes simultaneous excitation of electrons from filled states just below E_f to just above E_f. This phenomenon requires the presence of a high density of states at E_f a condition clearly fulfilled in U metal [Fig. 1(b)]. Calculations[6,7] also indicate a high density of empty states above E_f. In addition the bandwidth in U metal (~1.5 eV FWHM) is sufficient to cause the observed tailing in the U-metal 4*f* levels, particularly since both the cutoff required in the calculation of core-level line shapes[25] and the details of the calculation show that only the top 1 to 2 eV of the conduction-band density of states contributes significantly to the core-level asymmetry. This mechanism could contribute $\lesssim$0.5-eV broadening on the high-binding-energy side of all the observed core-level spectra, but it can not explain the additional broadening in UN which is discussed below. Because of the lack of detailed calculations for these compounds on such effects as configuration interaction, the discussion below is necessarily phenomenological, in the sense that the contributing sources of linewidths to UN are arrived at by comparison with the trends in the other compounds.

In UO_2, the entire *f* band is moved below E_f so this broadening mechanism should be removed. The 4*f* peaks are found to be quite symmetric with a width of ~2.5 eV. One source of additional broadening in UO_2 is multiplet splitting[26] as it is magnetic; i.e., the "magnetic" electrons are correlated. The lack of observable asymmetry implies, however, that the multiplet-splitting contribution is a small fraction of the total width (say, <0.5 eV). The observed broadening must therefore reflect a change in hole lifetime (unlikely to be this large a change), unresolved shake up (configuration interaction) or, more trivially, sample charging or heterogeneity in the sense that not all uranium is present as U^{4+} in UO_2. The features at $\Delta E = 6.0$ eV in UO_2 have been previously attributed to shake up.[23,27,28]

In UN several of the above broadening mechanisms are still available. The high density of states at E_f and the observed bandwidth could lead to asymmetric tailing of the order of magnitude observed in U metal (~0.5 eV). The effect of multiplet splitting is expected to be similar to or less than that in UO_2 because the magnetic moment of UN is less than that of UO_2. Therefore, neither of these effects could contribute sufficiently to explain the observed UN linewidth. The asymmetry in UN and the small width in U metal indicate that lifetime effects are not a dominant source of the UN linewidth. What is left by a process of elimination is configuration interaction, i.e., in UN there are a number of closely spaced final-state configurations that are not available in U metal, Th, and ThN. Photoemission measurements are sensitive not only to final-state-configuration interaction, but also to initial-state-configuration interaction, one example of which is mixed valency. Becuase of the time scale (10^{-16} s) of photoelectron spectroscopy, the presence of alternating valence should be detectable as distinct peaks in the spectra of core levels, as has been observed in CeN[21]. The chemical shift expected for unit valency change (e.g., $U^{3+} \rightarrow U^{4+}$) would be small,[29] only of the order of 1 eV. However, alternating valence in the initial state can be masked by larger final-state-configuration interaction which serves to broaden and merge the peaks from such initial-state configurations as may exist. In higher-resolution (0.9-eV) measurements of the

U $4f_{5/2}$ level (Mg-$K\alpha$ radiation), we have in fact detected a very weak shoulder at $\Delta E \sim 2$ eV.

In an attempt to detect effects of multiplet splitting in the different compounds, XPS measurements were made upon the U 6*s* levels in U, UN, and UO_2. Within our photon energy range only the 6*s* level gave a well-separated emission peak in the photoelectron spectrum. These spectra are illustrated in Fig. 4 and although the statistics are not as good as those obtained for the U 4*f* spectra (because of the inherently very low intensities of the lines) it is clear that the 6*s* lines are asymmetric, much broader than the 4*f* lines (FWHM of 5–6 eV), and similar for UN, U, and UO_2. The broadening is clearly too large to be a result of magnetic correlation and indeed is independent of the moment. Lifetime effects probably contribute significantly to the width because of the availability of Coster-Kronig deexcitation channels, but the asymmetry, which appears in all three compounds, must reflect the contribution from configuration interaction indicating that similar final-state configurations contribute in every case. These large broadening effects therefore mask any contribution to the 6*s* lines from multiplet splitting.

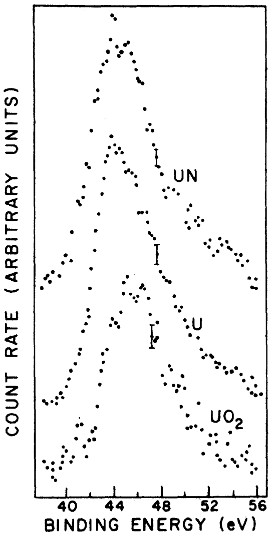

FIG. 4. 6*s* core-level photoemission spectra ($h\nu$ =1486.6 eV) of UN, U metal, and UO_2. Counting-statistic error limits for each spectrum are drawn as error bars. Peak-to-background ratios for spectra are ~0.05.

Because of the unusual magnetic properties of UN, particularly the fact that the ordered moment is only a small fraction of the paramagnetic moment, UPS measurements were made above and below $T_N \sim 50$ K to search for a possible temperature dependence of the *f*-state occupancy. No detectable change was observed between spectra obtained at 18, 77, and 298 K. Any band-structure changes must therefore be small.

Our photoemission results clarify the role of the *f* electrons in determining the magnetic properties of UN. They show conduction-band *f*-electron occupancy of 2.2 ± 0.5 electrons, compared with the 2.7 electrons calculated by Erbudak and Keller[6] who took account of spin polarization but not spin-orbit coupling and the ~2 electrons of the lowest 5*f* subband calculated by Adachi and Imoto[30] who took account of spin-orbit coupling but not spin polarization. More recent relativistic energy-band calculations[7] put the number of conduction-band *f* electrons at ~1.8. Experiment and band theory can thus account for the large paramagnetic moment (2.5 μ_B) and for the high specific-heat coefficient[31] (~20 states/eV). The low-ordered moment (0.75 μ_B) remains a mystery. We note that the self-consistent $T = 0$ K calculation of Ref. 6 produces too large an ordered moment (2.02 μ_B), suggesting that neglect of the spin-orbit splitting is possibly unwarranted. It is possible, however, that the effective number of electrons contributing to the paramagnetic susceptibility $\chi(q=0)$, which corresponds to direct electronic transitions, is much larger than the number of electrons associated with the antiferromagnetic ordering at wave vector $\vec{q} = (0,0,1)2\pi/a$. The *q* dependence of the susceptibility is also required to account for the anisotropy of the critical neutron scattering[32] and the large spin-wave energy gap.[33] It will therefore be essential to include the coupling of the *f* electrons to the other electron bands in any realistic description of uranium nitride.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating discussions with Dr. G. H. Lander who suggested this study and provided the UN sample. We also wish to acknowledge the technical help of J. W. Goodale.

---

[1] *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby (Academic, New York, 1974).

[2] G. H. Lander, AIP Conf. Proc. 29, 311 (1976); and in *Crystalline Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum, New York, 1977), p. 213.

[3] H. H. Hill, *Plutonium and Other Actinides*, edited by W. N. Miner (American Institute of Mining, Metallur-

gical, and Petroleum Engineers, New York, 1970), p. 2.

[4] R. Troc, J. Solid State Chem. 13, 14 (1975); P. de V. Du Plessis, C. F. Van Doorn, Physica (Utrecht) 86–88B, 993 (1977).

[5] N. A. Curry, Proc. Phys. Soc. London 86, 1193 (1965).

[6] M. Erbudak and J. Keller, Z. Phys. B32, 281 (1979).

[7] M. S. S. Brooks and D. Glötzel, Proceedings of the International Conference on Magnetism, Munich, 1979, J. Magnetism and Mag. Materials. (to be published).

[8] G. H. Lander, M. H. Mueller, D. M. Sparlin, and O. Vogt, Phys. Rev. B 14, 5035 (1976).

[9] W. H. Zachariasen, *The Law of Mass Action, a Centenary Volume* (Universitets Forlaget, Oslo, 1964), p. 185.

[10] P. R. Norton, Surf. Sci. 47, 98 (1975).

[11] J. F. Counsell, R. M. Dell, and J. F. Martin, Trans. Faraday Soc. 62, 1736 (1966).

[12] B. W. Veal and D. J. Lam, Phys. Lett. 49A, 466 (1974).

[13] J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. 8, 129 (1976).

[14] J. C. Fuggle, A. F. Burr, L. M. Watson, D. J. Fabian, and W. Lang, J. Phys. F 4, 335 (1974).

[15] H. L. Davis, *Plutonium 1970 and Other Actinides*, edited by W. N. Miner (AIME, New York, 1970), p. 209.

[16] G. H. Lander, S. K. Sinha, R. M. Sparlin, and O. Vogt, Phys. Rev. Lett. 40, 523 (1978).

[17] D. Eastman and M. Kuznietz, Phys. Rev. Lett. 26, 846 (1971).

[18] B. W. Veal and D. J. Lam, Phys. Rev. B 10, 4902 (1974).

[19] M. Erbudak and J. Keller, Phys. Rev. Lett. 42, 115 (1979).

[20] M. Campagna and G. K. Wertheim, in *Magnetism and Magnetic Materials—1974*, edited by C. F. Graham, Jr., G. H. Lander, and J. J. Rhyne (AIP, New York, 1974).

[21] Y. Baer and Ch. Zürcher, Phys. Rev. Lett. 39, 956 (1977).

[22] C. M. Varma, Rev. Mod. Phys. 48, 219 (1976).

[23] G. C. Allen and P. M. Tucker, Chem. Phys. Lett. 43, 254 (1976).

[24] G. M. Bancroft, T. K. Sham, and Sven Larson, Chem. Phys. Lett. 46, 551 (1977).

[25] G. K. Wertheim and P. H. Citrin, in *Optics in Applied Physics*, edited by M. Cardona and L. Ley (Springer, New York, 1978), Vol. XXVI, p. 197.

[26] C. Keller and C. K. Jorgensen, Chem. Phys. Lett. 32, 397 (1975).

[27] C. Miyake, H. Sakuri, and S. Imoto, Chem. Phys. Lett. 36, 158 (1975).

[28] J. J. Pireaux, J. Riga, E. Thibaut, C. Tenret-Noël, R. Caudano, and J. J. Verbist, Chem. Phys. 22, 113 (1977).

[29] T. A. Carlson, *Photoelectron and Auger Spectroscopy* (Plenum, New York, 1975), p. 374.

[30] H. Adachi and S. Imoto, J. Nucl. Sci. Technol. 6, 371 (1969).

[31] J. O. Scarbrough, H. L. Davis, W. Fulkerson, and J. O. Bettenton, Phys. Rev. 176, 606 (1968).

[32] W. J. L. Buyers, T. M. Holden, E. C. Svensson, and G. H. Lander, *Neutron Irradiation Scattering 1977* (International Atomic Energy Agency, Vienna, 1978), Vol. II, p. 239.

[33] T. M. Holden, E. C. Svensson, W. J. L. Buyers, and G. H. Lander, J. Phys. Paris 40, C4-31 (1979).