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Theoretical and experimental electronic structure of Zr-based transition-metal glasses containing Fe, Co, Ni, Cu, Rh, and Pd

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Measured valence-band photoelectron spectra for the transition-metal glasses $A_x\text{Zr}_{100-x}$ (A = Fe, Co, Ni, Cu, Rh, and Pd, with x approximately 25) are shown to be in good agreement with self-consistent energy-band state densities for ordered compounds in the AuCu_3 (fcc-like) crystal structure. The calculations and measurements both yield high Fermi-level state densities, account for core-level line shapes, and are consistent with the occurrence of superconductivity and with trends in the transition temperatures of glassy alloys of Zr with $3d$ transition metals.

INTRODUCTION

The correct identification of structure in photoelectron spectra is greatly facilitated by electronic structure calculations. Such calculations are difficult for metallic glasses because the absence of long-range order makes the relevance of energy-band calculations questionable. Each of the available calculational options in this context, molecular-cluster, coherent-potential, and energy-band calculations, has its advantages and disadvantages. The fundamental facts underlying our choice of energy-band calculations to study these materials are as follows: (1) The dominant (slowly varying) structure in the state density given by an energy-band calculation is due primarily to the nearest-neighbor chemical environment of each atom. (Rapidly varying detail in the state density can be associated with more distant neighbors.) (2) The interatomic bonding is treated without the approximations introduced by the statistical averaging approximations on which coherent-potential calculations are based. (3) The electrostatic implications of charge transfer are accurately treated. (4) The total energy can be accurately evaluated and used to determine the interatomic spacing appropriate to the single local arrangement of atoms considered in the energy-band calculation. Since our objective is to interpret the dominant features of photoemission spectra, band calculations appear to be a sensible tool. The purpose of this paper is to show that band calculations for ordered alloys are in good agreement with measurements on transition-metal glasses and, therefore, provide a useful interpretation of the measurements.

Studies on a wide range of transition-metal systems using extended x-ray-absorption fine-structure,[1] diffraction,[2] and NMR (Ref. 3) measurements all yield a clear indication that both structural and chemical short-range order is present in the metallic glasses. In addition, comparison of experimental valence-band spectra for disordered and crystalline phases of the same system yield electronic structures with gross features which are in essential agreement.[4] For these reasons we expect that band-structure calculations for ordered alloys can provide a good approximation of the electronic structure of transition-metal glasses. Experimentally, these systems have high coordination numbers[5] and can, therefore, be expected to be similar to appropriate close-packed, fcc-like model structures of corresponding stoichiometry.

Zirconium-based transition-metal glasses are relatively easy to form and have been extensively studied.[6] Glassy $A_x\text{Zr}_{100-x}$, where A = Fe, Co, Ni, Cu, Rh, and Pd, with x approximately 25, constitutes an interesting series which exhibits both superconducting and magnetic properties. This paper makes use of theoretical energy-band calculations to study the trends in the properties of this series.

The calculations used in this paper employ the local-density approximation to electronic exchange and correlation and the augmented–spherical-wave method[7] for the self-consistent solution of the single-particle equations. The calculated state densities appearing in Figs. 1–6 correspond to the lattice constant for which the calculated total energy is a minimum. For systems obeying Vegard's law, the volume of the alloy unit cell is simply the sum of the volumes of the constituent atomic cells, and the partitioning of the alloy unit cell into atomic cells is accomplished by leaving the constituent atomic-cell size unchanged. Since Vegard's law is not assumed in our calculations, the alloy atomic cells must be changed slightly. As mentioned above, the total (unit-cell) volume change is given by total-energy minimization. We distribute the total volume change among the atomic cells in proportion to the compressibility of each constituent. With this partitioning strategy, the inputs to the calculations become only the constituent atomic numbers and the crystal structure.

RESULTS

Figures 1–6 compare measured ultraviolet photoemission spectroscopy (UPS) spectra for a series of glassy Zr alloys close to the 1–3 stoichiometry[4] with calculated state densities for comparable ordered compounds in the $AuCu_3$ structure. From the sequence it is obvious that the UPS valence bands are closely related to the density of states for the ordered structure. The main results of the comparison

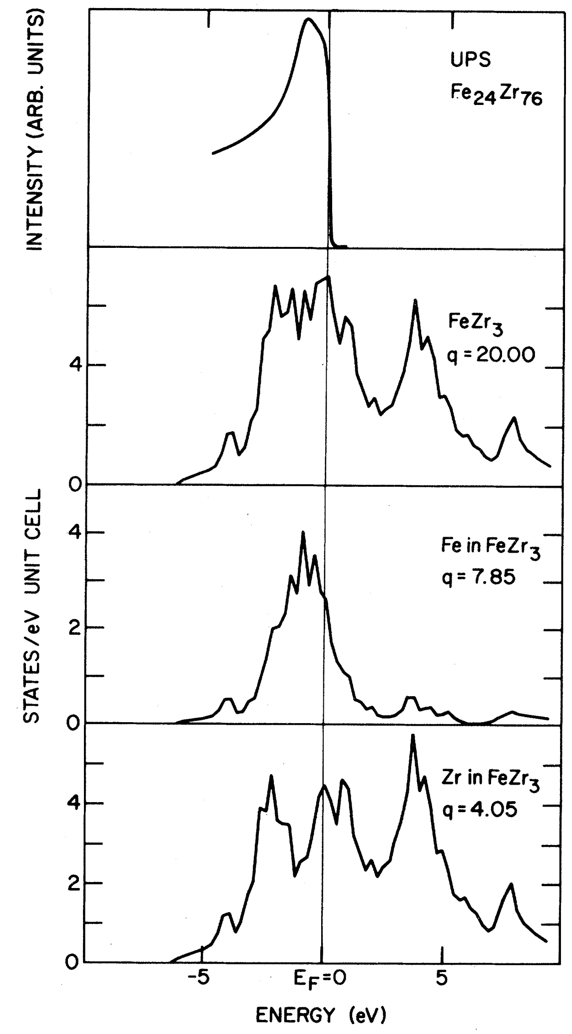

FIG. 1. Valence-band spectrum ($h\nu=21.2$ eV) of glassy $Fe_{24}Zr_{76}$ and calculated state densities (total and site decomposed) for $FeZr_3$ ($AuCu_3$ structure). q is the charge per unit cell and charge per site, respectively. The d charge transfers are + 0.04 and −0.02 for Fe and Zr, respectively.

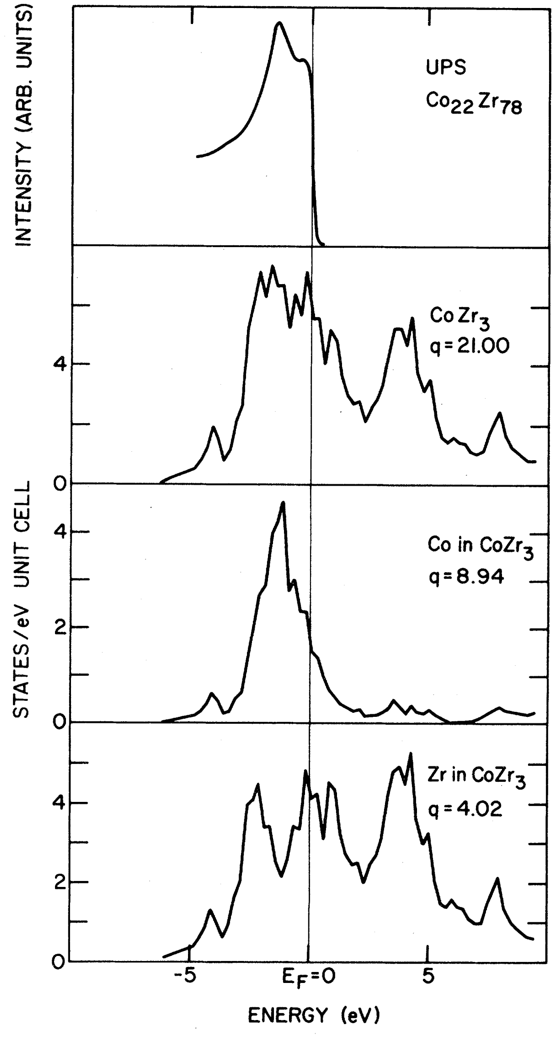

FIG. 2. Valence-band spectrum ($h\nu=21.2$ eV) of glassy $Co_{22}Zr_{78}$ and calculated state densities (total and site decomposed) for $CoZr_3$ ($AuCu_3$ structure). q is the charge per unit cell and charge per site, respectively. The d charge transfers are + 0.01 and −0.02 for Co and Zr, respectively.

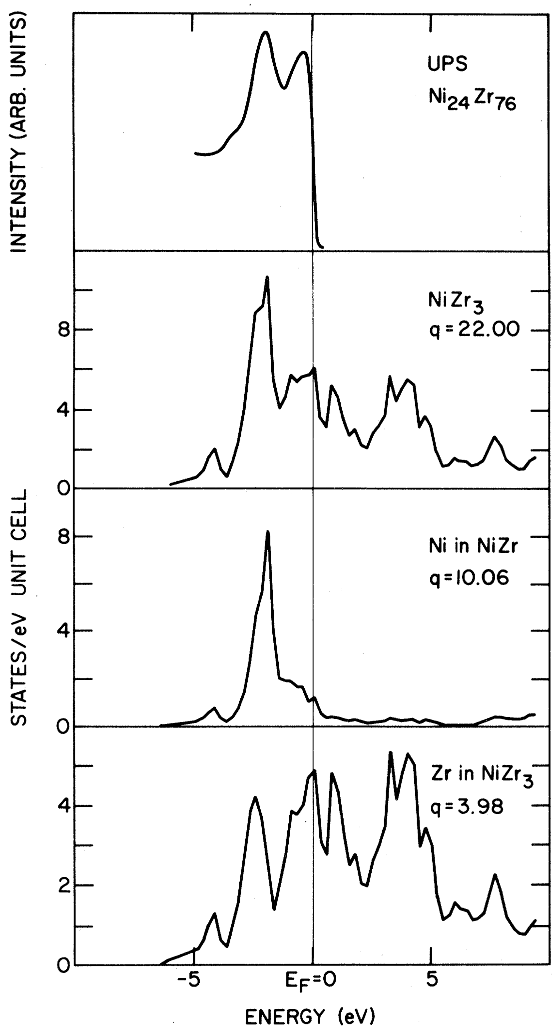

FIG. 3. Valence-band spectrum ($h\nu=21.2$ eV) of glassy $Ni_{24}Zr_{76}$ and calculated state densities (total and site decomposed) for $NiZr_3$ ($AuCu_3$ structure). q is the charge per unit cell and charge per site, respectively. The d charge transfers are -0.04 and -0.02 for Ni and Zr, respectively.

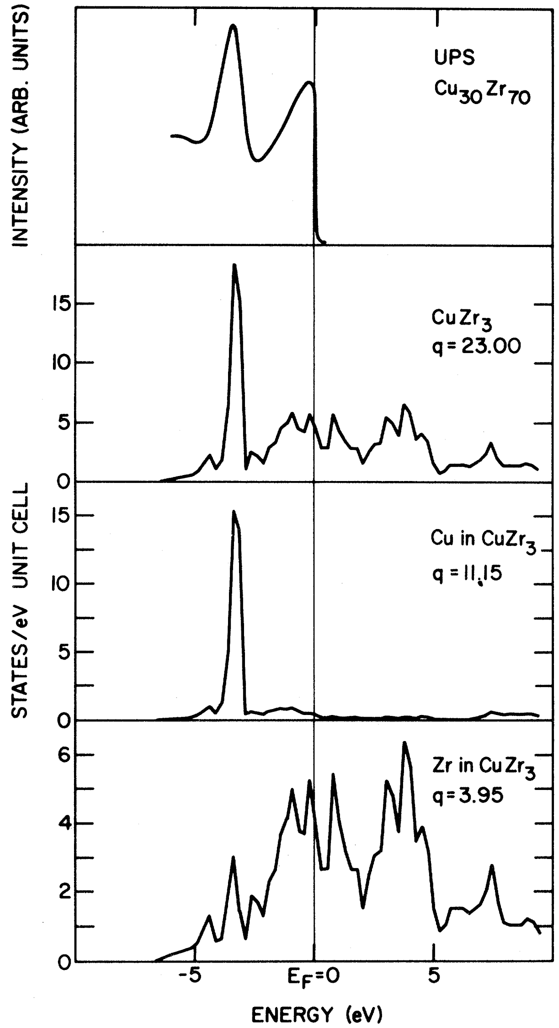

FIG. 4. Valence-band spectrum ($h\nu=21.2$ eV) of glassy $Cu_{30}Zr_{70}$ and calculated state densities (total and site decomposed) for $CuZr_3$ ($AuCu_3$ structure). q is the charge per unit cell and charge per site, respectively. The d charge transfers are -0.12 and $+0.01$ for Cu and Zr, respectively.

of the experimental and theoretical results are summarized in the following points:

(1) The measured d-band peak position, corresponding to the d states of the late transition metal, is in agreement with the calculated values to within 0.2 eV. (In the case of $Co_{22}Zr_{78}$, the deviation can be explained by the slight difference in alloy composition.)

(2) The calculations clearly show the *decrease* of state densities on the late transition-metal site at the Fermi level (with the exception of $CuZr_3$). This decrease explains the observed decrease of the late transition-metal core-level line asymmetry on alloying (Table I).

(3) The electronic properties at the Fermi level are *dominated* by Zr d states (even in $FeZr_3$ which has an appreciable contribution of Fe $3d$ states at the Fermi level).

(4) The $PdZr_3$, $RhZr_3$, and $CuZr_3$ calculations show a splitting of the Zr d bands which is not present in pure Zr. This splitting has been experimentally confirmed by x-ray-emission spectroscopy for $Pd_{30}Zr_{70}$ by Hague *et al.*,[8] and by means of Auger electron spectroscopy (AES) for Pd-Zr and Rh-Zr alloys by Oelhafen *et al.*[9]

(5) The photoionization cross section σ of the late

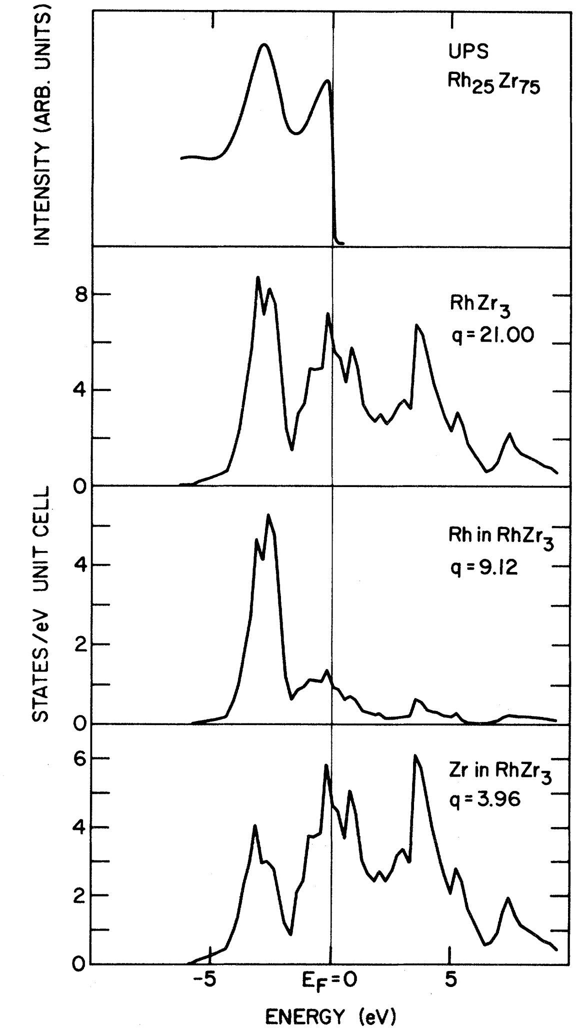

FIG. 5. Valence-band spectrum ($h\nu=21.2$ eV) of glassy $Rh_{25}Zr_{75}$ and calculated state densities (total and site decomposed) for $RhZr_3$ ($AuCu_3$ structure). q is the charge per unit cell and charge per site, respectively. The d charge transfers are $+0.12$ and -0.07 for Rh and Zr, respectively.

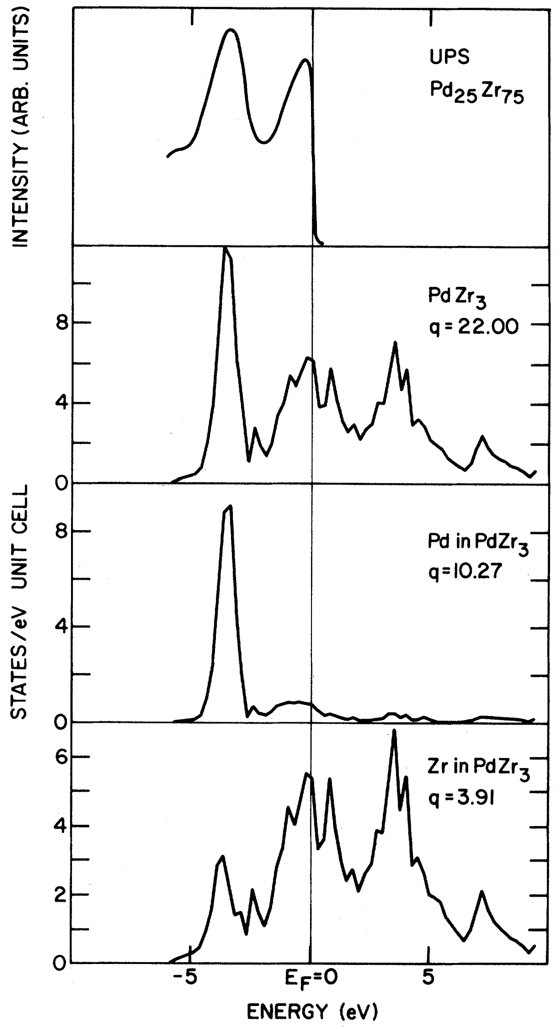

FIG. 6. Valence-band spectrum ($h\nu=21.2$ eV) of glassy $Pd_{25}Zr_{75}$ and calculated state densities (total and site decomposed) for $PdZr_3$ ($AuCu_3$ structure). q is the charge per unit cell and charge per site, respectively. The d charge transfers are -0.04 and -0.07 for Rh and Zr, respectively.

TABLE I. Core-level binding-energy shifts ΔE_B, relative to the pure constituents, for glassy Zr-based transition-metal alloys (accuracy ±0.1 eV). The asymmetry change $\Delta\alpha$ of the core lines on alloying is indicated by + or − for an increase or a decrease, respectively.

Alloy	Level	ΔE_B (eV)	$\Delta\alpha$	Level	ΔE_B (eV)	$\Delta\alpha$	Reference
$Fe_{24}Zr_{76}$	Fe $2p_{3/2}$	0.05	−	Zr $3d_{5/2}$	0.10	+	18
$Co_{40}Zr_{60}$	Co $2p_{3/2}$	0.00	−	Zr $3d_{5/2}$	0.11	+	18
$Ni_{37}Zr_{63}$	Ni $2p_{3/2}$	0.55	−	Zr $3d_{5/2}$	0.05	+	18
$Cu_{30}Zr_{70}$	Cu $2p_{3/2}$	0.45	+	Zr $3d_{5/2}$	0.00	+	23
$Rh_{25}Zr_{75}$	Rh $3d_{5/2}$	0.17	−	Zr $3d_{5/2}$	0.14	+	18
$Pd_{30}Zr_{70}$	Pd $3d_{5/2}$	1.50	−	Zr $3d_{5/2}$	0.20	+	10

transition-metal d states relative to that of Zr for He I ($h\nu = 21.2$ eV) excitation is *decreasing* appreciably in the $3d$ series going from Fe to Cu. In $Fe_{24}Zr_{76}$, the UPS spectrum is dominated by the Fe $3d$ states, with almost no contribution from the Zr states. The $3d$ contribution relative to that of the Zr $4d$ decreases for $Co_{22}Zr_{78}$ and $Ni_{24}Zr_{76}$, whereas in $Cu_{30}Zr_{70}$ the excitation cross section for Cu $3d$ and Zr $4d$ states are about equal. [The calculated state density presented here is more similar to the measured photoemission spectrum than a state density published previously by Kübler *et al.*[10] The origin of the difference between the two calculated state densities is the volume (lattice constant) at which the two calculations were performed and the strategy used to partition the alloy unit cell into atomic cells.]

DISCUSSION

A general feature of all our calculated and measured results is the location of the Fermi level at, or near, a maximum in the density of states.[11] A high Fermi-level state density $n(E_F)$ is usually an indication that a system is not particularly stable and that it can lower its total energy by undergoing a structural transition or a transition to either a superconducting or a magnetic state. For the systems considered here, the choice is between superconductivity and magnetism and depends upon the details of the electron-phonon and magnetic interactions.

Superconductivity in Zr-based metallic glasses with Cu, Ni, Co, Fe, Mn, Cr, V, Rh, and Pd has been discussed by Tennhover and Johnson[12] who related the superconducting transition temperatures, T_c, to $n(E_F)$. Using a Varma-Dynes[13] analysis, they showed that these glassy superconductors behaved much like the crystalline superconductors and that T_c and $n(E_F)$ are simply related, with T_c increasing with increasing $n(E_F)$. By using measured values of the perpendicular critical field, normal-state resistivity, and photoelectron valence-band spectra, the $n(E_F)$ increase for the sequence Zr-(Cu, Ni, Co, Fe) was qualitatively explained in terms of the different binding energies of the d bands of the late transition metals. Our state-density calculations (Figs. 1—6 and Table II) confirm this picture and show that the Zr $4d$ contribution to $n(E_F)$ is roughly constant while the $3d$ contribution from the late transition metal is increasing in going from Cu to Fe. Tennhover and Johnson[12] also pointed out that the trend in T_c is broken for Zr alloys with elements to the left of Co, and explained this behavior by postulating the occurrence of spin fluctuations and the formation of localized magnetic moments at sites of the $3d$ elements. Since both of these effects act as pair-breaking mechanisms, they lead to a depression of T_c. Our electronic structure calculations on amorphous Zr alloys with Mn, Cr, and V confirm this picture and are discussed elsewhere.[14]

TABLE II. Superconducting transition temperature T_c of Zr-based glassy transition-metal alloys.

Glassy alloy	T_c (K)	Reference
$Fe_{30}Zr_{70}$	1.9	11
$Co_{30}Zr_{70}$	3.3	19
$Ni_{30}Zr_{70}$	2.9	19
$Cu_{30}Zr_{70}$	2.8	20
$Rh_{23}Zr_{77}$	4.1	21
$Pd_{30}Zr_{70}$	2.7	22

TABLE III. Total and site decomposed calculated Fermi-level state densities (states/eV atom) for Zr-based glassy transition-metal alloys.

AZr_3 alloy	A site	Zr site	Total
$FeZr_3$	2.66	1.47	1.77
$CoZr_3$	1.75	1.43	1.51
$NiZr_3$	1.14	1.62	1.50
$CuZr_3$	0.41	1.43	1.18
$RhZr_3$	1.07	1.66	1.51
$PdZr_3$	0.78	1.82	1.56

Note that the T_c values listed in Table II are characteristic of disordered transition-metal systems. That is, they do not agree with the Matthias rule[15] for crystalline transition-metal compounds which correlates T_c with the electron per atom ratio. The ratios for the alloys listed here are all between 5.1 and 6.1. According to the Matthias rule, T_c should be low and going through a minimum. The high T_c values shown here are consistent with the results of Collver and Hammond[16] and are a consequence of the high Fermi-level state density (Figs. 1—6) for these systems.

The core-electron binding-energy shifts ΔE_B relative to the pure constituents and the changes in line asymmetry $\Delta\alpha$ for the most intense core lines are given in Table III. Except for the Pd $3d_{5/2}$ line, the binding-energy shifts are relatively small (0.55 eV or less), indicating that there is little charge transfer with alloying. This is in agreement with our band-structure calculations (Figs. 1—6) which show very little change in d-electron charge upon alloying.

The asymmetry change of the core lines are included in Table I where plus and minus signs represent an increase and a decrease in asymmetry, respectively. As discussed earlier,[14] the asymmetry provides, to some extent, a local probe of the Fermi-level state density. Except for the case of the noble metal Cu the asymmetry strongly decreases for the late transition metals, indicating a decrease of the late transition-metal contribution to $n(E_F)$. The increase in asymmetry for Zr indicates that Zr has a higher $n(E_F)$ in the alloys than in the elemental form. This is due to the location of E_F near a minimum in the state density for pure Zr.[17]

CONCLUSION

We conclude that band-structure calculations for ordered alloys are in good agreement with measurements on disordered transition-metal systems and are, therefore, useful for interpreting the measurements. They can successfully account for the core-level line shapes and for the trends in superconducting temperatures.

ACKNOWLEDGMENT

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