Electronic and magnetic properties of the kagomé systems $\text{YBaCo}_3\text{O}_7$ and $\text{YBaCo}_3\text{MO}_7$ ($M=\text{Al, Fe}$)

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We present a combined experimental and theoretical x-ray absorption spectroscopy (XAS) study of the new class of cobaltates $\text{YBaCo}_4\text{O}_7$ and $\text{YBaCo}_3\text{MO}_7$ ($M=\text{Al, Fe}$). The focus is on the local electronic and magnetic properties of the transition metal ions in these geometrically frustrated kagomé compounds. They show a rich collection of interesting physical phenomena, including superconductivity, giant magneto resistance, temperature-driven spin-state and metal-insulator transitions, as well as spin-blockade behavior.

These astonishing physical effects are directly related to the charge, orbital, and spin degrees of freedom of the Co ions.

Cobaltates are currently one of the most investigated classes of transition metal oxides. They show a rich collection of interesting physical phenomena, including superconductivity, giant magneto resistance, strong thermopower, temperature-driven spin-state and metal-insulator transitions, as well as spin-blockade behavior. These astonishing physical effects are directly related to the charge, orbital, and spin degrees of freedom of the Co ions.

Some cobaltates also show a high degree of magnetic frustration. Recently, a new class of cobaltates was introduced with the compound $\text{YBaCo}_4\text{O}_7$, which contains kagomé layers of tetrahedrally coordinated Co. The strong antiferromagnetic interactions combined with the geometry in the lattice in these compounds lead to magnetic frustration. It is most important to understand the local electronic and magnetic properties of such frustrated systems in order to model their magnetic behavior.

Yet, very different values are suggested in the literature concerning the magnetic moments in $\text{YBaCo}_4\text{O}_7$. The first susceptibility measurements yielded the large number of $5.8\mu_B$ per magnetic ion, but later experiments gave only $2.2\mu_B$. One neutron study estimated $\mu_t = 3.49\mu_B$ for the ordered moment in the triangular layer and $\mu_k = 2.19\mu_B$ in the kagomé lattice, while another reported $\mu_t = 1.66\mu_B$ and $\mu_k = 1.68\mu_B$, respectively. It is perhaps a priori also not very clear what moments to expect theoretically since it is known, for example, that a Co$^{3+}$ ion has the so-called spin state degree of freedom: it can be low spin (LS, $S=0$, non-magnetic), intermediate spin (IS, $S=1$) or high spin (HS, $S=2$), depending on the details of the local crystal field.

Here we present a study of the local electronic properties of $\text{YBaCo}_4\text{O}_7$, and its variants $\text{YBaCo}_3\text{AlO}_7$ and $\text{YBaCo}_3\text{FeO}_7$, using soft x-ray absorption spectroscopy (XAS) at the Co and Fe $L_{2,3}$ edges. We critically examine the charge state of the ions as well as their separate orbital and spin contributions to the magnetic moment.

Single crystals of $\text{YBaCo}_3\text{FeO}_7$ and $\text{YBaCo}_3\text{AlO}_7$ were prepared by the floating zone technique in an image furnace. For the pure cobaltate $\text{YBaCo}_4\text{O}_7$, a solid-state reaction was used to obtain polycrystalline samples. All samples have been characterized by x-ray diffraction, magnetic measurements and electrical resistivity which are published elsewhere. The materials are insulators and show highly frustrated magnetic properties. The XAS experiments were carried out at the Dragon Beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan with an energy resolution of about 0.3 eV. The degree of linear polarization of the incident light was ~ 99%. Clean sample areas were obtained by cleaving the crystals in situ at pressures in the low 10$^{-10}$ mbar range. The absorption of the $L_{2,3}$ edges of Co and Fe was recorded using the total electron yield method. The oxygen K edge XAS was also measured by using both the total electron and fluorescence yield method. The fluorescence detector was manufactured by Quantar Technology and is equipped with a grid and bias voltages to reject ions and electrons. CoO and Fe$_2$O$_3$ single crystals were also measured simultaneously to serve as energy reference for the Co and Fe $L_{2,3}$ edges, respectively.

Fig. contains the Co $L_{2,3}$ XAS spectra of $\text{YBaCo}_3\text{AlO}_7$, $\text{YBaCo}_3\text{FeO}_7$, and $\text{YBaCo}_4\text{O}_7$. The spectra are the result of the dipole-allowed Co $2p^63d^n \rightarrow 2p^53d^{n+1}$ absorption process. The spin-orbit coupling of the 2p core hole causes the largest splitting in the spectra: the appearance of the distinct $L_3$ ($\approx 780$ eV) and $L_2$ ($\approx 795$ eV) white lines can be associated with the $2p_{3/2}$ and $2p_{1/2}$ core hole final states, respectively. The intense peaks at about 5 eV above the Co white lines represent the $M_{4,5}$ absorption lines of barium, i.e. the Ba $3d^{10}4f^{93} \rightarrow 3d^{10}4f^{13}$ transitions. As the cobalt is of interest, we need to subtract the Ba signal using a
FIG. 1: (color online) Experimental Co $L_{2,3}$ XAS spectra of YBaCo$_3$AlO$_7$, YBaCo$_3$FeO$_7$, and YBaCo$_4$O$_7$. The YBaZn$_3$AlO$_7$ spectrum shown at the bottom serves as a reference for the Ba $M_{4,5}$ edges. The inset depicts the oxygen K XAS spectrum of YBaCo$_4$O$_7$ collected by the total electron yield (TEY) and fluorescence yield (FY) methods.

reference material. For this the isostructural compound YBaZn$_3$AlO$_7$ was synthesized. Its Ba $M_{4,5}$ spectrum is shown at the bottom of Fig. 1. The inset displays the oxygen K XAS spectrum of YBaCo$_4$O$_7$ measured in total electron yield and fluorescence yield mode. The close similarity of the spectra collected by these two methods confirms that our measurements are indeed representative for the bulk material and are not plagued by possible surface effects.

Fig. 2 shows the Co $L_{2,3}$ edge spectra with the Ba $M_{4,5}$ signal subtracted. Remnants of the subtraction produce small glitches at around 785 and 799 eV and are omitted from the curves. It can be seen that the spectra of YBaCo$_3$AlO$_7$ and YBaCo$_3$FeO$_7$ are practically identical, and that they are different from that of YBaCo$_4$O$_7$. We have also investigated the possible dependence of the spectra on the polarization of the light, but we found no indications for linear dichroism in these YBaCo$_3$AlO$_7$ and YBaCo$_3$FeO$_7$ compounds. It is interesting to note that all these spectra are very different from the ones reported for the more known Co compounds with CoO$_6$ coordination like CoO$_{19,20}$, LaCoO$_{12}$, LaMn$_{0.5}$Co$_{0.5}$O$_{21}$, Ca$_3$Co$_2$O$_6^{22}$, Ca$_3$CoRhO$_6^{28}$, and La$_{1.5}$Sr$_{0.5}$CoO$_{4.8}$.  

We first focus on the Co spectrum of YBaCo$_3$AlO$_7$. From the chemical formula, for which Al is known to be very stable as a non-magnetic trivalent ion, one is expecting the Co to be in the divalent state. The fact that its spectrum is quite different from that of the divalent Co in CoO, must be sought in the very different local coordination: tetrahedral in YBaCo$_3$AlO$_7$ and octahedral in CoO. To prove this conjecture, we have carried out a simulation based on the successful configuration interaction cluster model that includes the full atomic multiplet theory and the local effects of the solids. It accounts for the intra-atomic Co 3$d$-3$d$ and 2$p$-3$d$ Coulomb and exchange interactions, the atomic 2$p$ and 3$d$ spin-orbit couplings, the O 2$p$ - Co 3$d$ hybridization, and the local crystal field. Here we set up a CoO$_4$ cluster in $T_d$ symmetry and used a negative value for the crystal field parameter $10Dq$ to represent the splitting between the low two-fold $e$ and the high three-fold $t_2$ orbitals. The cluster model calculations were done using XTLS 8.3.
The parameter values are based on those already known for bulk CoO. The strength of the O 2p - Co 3d hybridization was estimated using Harrison’s description for the experimental value of the Co-O bond length. The $10Dq$ value was tuned to fit the experimental spectrum. The simulation result is shown as the middle curve in Fig. 2. The model excellently matches the experimental spectrum. The negative value of $10Dq = -0.15$ eV, needed in the simulation, confirms the $T_d$ symmetry of the local coordination of Co$^{2+}$ in YBaCo$_3$AlO$_7$. The lack of any polarization dependence in the experiment is also fully consistent with the completely filled $t_2$ shell for a Co$^{2+}$ ion in perfect $T_d$.

The striking similarity between the YBaCo$_3$Fe$_7$ spectrum with that of YBaCo$_3$AlO$_7$ suggests that all the Co ions are also divalent in YBaCo$_3$FeO$_7$. To fulfill the charge balance, the Fe ions must be trivalent. To confirm this, we have carried out XAS measurements on the Fe $L_{2,3}$ edges. The results are shown in Fig. 3 along with a reference for Fe$^{2+}$ measured on FeO, and Fe$^{3+}$ taken from the Fe$_2$O$_3$ single crystal. The Fe spectrum of YBaCo$_3$Fe$_7$ is quite different from that of FeO. It is also appreciably dissimilar from that of Fe$_2$O$_3$, although the energy positions match quite well, strongly suggesting that Fe in YBaCo$_3$FeO$_7$ could indeed be trivalent. Similar to the case with Co, these deviations are caused by the fact that the local coordination is different: $T_d$ in YBaCo$_3$FeO$_7$ vs. $O_h$ in Fe$_2$O$_3$. To clarify this point, we have carried out simulations for an Fe$^{3+}$ ion in $T_d$ symmetry, and the result is shown at the bottom of Fig. 3. The experimental spectrum can be excellently reproduced. This thus confirms that the Fe is trivalent.

The parameter values used are reasonable with a negative $10Dq$ ($-0.35$ eV) for a $T_d$ local coordination.

We now return to the Co spectrum of YBaCo$_4$O$_7$, which is a mixed valent compound, with a relation of 3:1 for Co$^{2+}$:Co$^{3+}$ as expected from the chemical formula. Here, the spectrum is constructed as an incoherent sum of the Co$^{2+}$ and Co$^{3+}$ simulations in $T_d$ symmetry, weighted in a 3:1 ratio. We note that taking the sum incoherently is a reasonable approximation because the YBaCo$_4$O$_7$ compound is an insulator. The final result is shown at the bottom of Fig. 2. The match between simulated and experimental spectra is very good. For this simulation we used the Co$^{2+}$ parameters found for the YBaCo$_3$AlO$_7$ compound, and we set the Co$^{3+}$ parameters such that the 3$d^9$ ion is in the high spin state (HS, $S=2$).

As already explained above, a Co$^{3+}$ ion can be HS, IS or LS depending on the details of the local crystal field. To study this aspect more in detail for the Co$^{3+}$ ion in YBaCo$_4$O$_7$, we first made a subtraction of the YBaCo$_4$O$_7$ spectrum with the YBaCo$_3$AlO$_7$ spectrum weighted in a 4:3 ratio. The resulting difference spectrum is plotted in Fig. 4 and is meant to represent the Co $L_{2,3}$ XAS spectrum of the Co$^{3+}$ ion in YBaCo$_4$O$_7$. We have carried out simulations for this Co$^{3+}$ ion in $T_d$ symmetry, and we have done so for the HS ($e^7t_{2g}^3, S=2$) and IS ($e^7t_{2g}^2, S=1$) cases, see Fig. 3. For the HS state, we have used $10Dq = -0.34$ eV, a modest and realistic value close to the -0.15 eV value found for the Co$^{2+}$ ion in the YBaCo$_3$AlO$_7$ compound. The simulation is almost equal to the experimental spectrum. To reach the IS situation, we have to increase in absolute sense the $10Dq$ value.

FIG. 3: (color online) XAS spectrum on the Fe $L_{2,3}$ edges of YBaCo$_3$FeO$_7$. Reference spectra of Fe$^{2+}$ in FeO ($O_h$) and Fe$^{3+}$ in Fe$_2$O$_3$ ($O_h$) are also given. The spectrum at the bottom is a simulation for Fe$^{3+}$ in $T_d$ symmetry.

FIG. 4: (color online) Experimental Co $L_{2,3}$ XAS spectrum of the Co$^{3+}$ ion in YBaCo$_4$O$_7$ as extracted from the subtraction of the YBaCo$_4$O$_7$ spectrum with the YBaCo$_3$AlO$_7$ one in a 4:3 weight ratio. Theoretical simulations for the Co$^{3+}$ ion in $T_d$ symmetry are also included for the high spin ($S=2$) and intermediate spin ($S=1$) state cases.
As will be explained later, the crossing between the HS and IS cases is at about 10Dq = -1.65 eV, a very large and rather unphysical number since it is larger than what one could encounter in an Oh coordination. For this particular IS simulation we have used -1.9 eV. The agreement with the experimental spectrum is reasonable, but there are distinct features in the simulation, such as the shoulder at 793 eV, which is not present in the experiment.

We have not shown simulations for the LS (e^4t^2_2, S=0) state, since in Td symmetry it is not possible to have the two spins of the t2 electrons to be antiparallel. For the LS state to be stabilized, one would need a very strong local distortion such that the xy orbital in the t2 shell is lowered by at least 0.7 eV with respect to the xz/yz to overcome the local Hund’s exchange interaction. There is no experimental evidence for such strong distortions. We therefore can conclude that the Co^{3+} ion in YBaCoO_7 is most likely in the HS state.

Having established the local electronic structure and having obtained reasonable estimates for the size of the crystal fields, we now will look at the consequences for the local magnetic properties of Co^{2+} and Co^{3+} in Td symmetry with the aid of full multiplet theory. The ground state of Co^{2+} in a tetrahedral crystal field is four-fold spin degenerate, as in first order the e subshell is completely filled and the t2 subshell half-filled giving S = 3/2, leaving no orbital degeneracy. This would also completely quench the orbital momentum. In second order, however, the on-site Coulomb and exchange interactions (multiplet effects) mix a certain amount of e electrons into the t2 shell and restore the orbital momentum partially. This mixing depends on the relative size of the ligand field splitting and the spin-orbit coupling and does not split the ground state. But its energy is lowered and the total magnetic moment is enhanced by the orbital momentum. While in octahedral complexes the ligand field is often strong enough to suppress such second order effects, they play a role in tetrahedral coordination. In the calculation for Co^{3+}, the amount of orbital momentum is 0.5µ_B, increasing of the total magnetic moment to 3.5µ_B. In a magnetic susceptibility measurement, the effective moment at room temperature extracted from the Curie-Weiss law would be µ_{eff} = 4.6µ_B (the spin-only value is 3.9µ_B).

FIG. 5: Energy level diagrams for Co^{2+} in a tetrahedral crystal field (panel (a), Td, negative 10Dq) and octahedral crystal field (panel (b), Oh, positive 10Dq). The full-multiplet calculations include covalency due to O 2p - Co 3d hybridization.

FIG. 6: Energy level diagrams for Co^{3+} in a tetrahedral crystal field (panel (a), Td, negative 10Dq) and octahedral crystal field (panel (b), Oh, positive 10Dq). The full-multiplet calculations include covalency due to O 2p - Co 3d hybridization.
splitting in $T_d$ is generally smaller than in $O_h$ for identical bonding lengths between metal and ligand ions, as it can be seen from point charge calculations that $Dq(T_d) = -\frac{1}{4}Dq(O_h)$\textsuperscript{29}.

The influence of the spin-orbit coupling on the Co$^{3+}$ spin-state has been studied in detail for the octahedral case\textsuperscript{2}. It was found that it plays a decisive role for the magnetic properties of LaCoO$_3$: the HS state with $S=2$ is split in three sublevels with $J = 1, 2, 3$, the lowest of which is 3-fold degenerate and not 5-fold as expected for a $S=2$. By contrast, the IS state with $S=1$ is split into $J = 2, 1, 0$, resulting in a lowest state which is 5-fold degenerate and not 3-fold as expected for a $S=1$.

Recognizing these true degeneracies resolved much of the confusion concerning the interpretation of the magnetic susceptibility data\textsuperscript{22}. The situation for a Co$^{3+}$ ion in $T_d$ is rather different. The stable HS with $S=2$ state is a 10-fold degenerate $^5E$ state if the spin-orbit coupling effects were absent. The presence of spin-orbit interactions will split this state into 4 singlets and 3 doublets. The energy splitting however, is rather small, not much larger than 15-20 meV in total, see inset in Fig. 6. For temperatures lower than about 20K, the magnetic susceptibility will be quite complicated and will depend strongly on the magnitude of the applied field or effective molecular field in the solid. In the high temperature regime, the magnetic susceptibility will be Curie-Weiss like corresponding to a $^5\!E$ ion. The effective moment at 300K is then estimated to be $\mu_{eff} = 5.1 \mu_B$, close to the spin-only value of 4.9$\mu_B$. The total effective moment estimated for YBaCo$_4$O$_7$ is $\left(\frac{1}{4}(4.6\mu_B)^2 + \frac{1}{2}(5.1\mu_B)^2\right)^{1/2} = 4.7\mu_B$ per Co ion. If these moments would be ferromagnetically ordered without frustration, the ordered moment is $\frac{2}{3}3.5\mu_B + \frac{1}{4}4\mu_B = 3.6\mu_B$.

To summarize, we have investigated the electronic properties of YBaCo$_3$AlO$_7$, YBaCo$_3$FeO$_7$, and YBaCo$_3$O$_7$ in detail. This was done by the use of XAS spectroscopy and the comparison to configuration interaction calculations. We have obtained estimates for the crystal fields and have determined the charge and spin states of the relevant ions. These findings allowed us to analyze reliably the local magnetic properties: in $T_d$ symmetry the Co$^{2+}$ ions have essentially the $S=3/2$ configuration, while the Co$^{3+}$ are in the high spin $S=2$ state. The reduced ordered moment of Co in YBaCo$_3$O$_7$ as seen from neutron scattering must therefore be related to magnetic frustration. Spin-orbit effects do induce an orbital moment in the magnetism of Co$^{2+}$ in all three compounds, but will not lead to a large magnetic anisotropy as the tetrahedral structure is almost regular. For Co$^{3+}$, the spin-orbit induced splitting of the $S=2$ manifold could lead to an intriguing low temperature magnetic behavior. For the YBaCo$_3$FeO$_7$ compound, we have determined the Fe charge state to be Fe$^{3+}$, meaning that Fe will act as a magnetic ion with spin-only moment in the compound. Evidently, this family of cobaltates is a good basis to study strongly interacting moments on a kagomé lattice.

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\textsuperscript{1} K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) \textbf{422}, 53 (2003).
\textsuperscript{2} J. Perez, J. Garcia, J. Blasco, and J. Stankiewicz, Phys. Rev. Lett. \textbf{80}, 2401 (1998).
\textsuperscript{3} I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B \textbf{56}, R12685 (1997).
\textsuperscript{4} P.M. Raccah and J.B. Goodenough, Phys. Rev. \textbf{155}, 932 (1967).
\textsuperscript{5} A. Maignan, V. Caignaert, B. Raveau, D. Khomskii, and G. Sawatzky, Phys. Rev. Lett. \textbf{93}, 026401 (2004).
\textsuperscript{6} C. F. Chang, Z. Hu, H. Wu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H. H. Hsieh, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. \textbf{102}, 116401 (2009).
\textsuperscript{7} A. Maignan, C. Michel, A. C. Masset, C. Martin, and B. Raveau, Eur. J. Phys. B \textbf{5}, 657 (2000).
\textsuperscript{8} N. Rogado, G. Lawes, D. A. Huse, A. P. Ramirez, and R. J. Cava, Solid State Commun. \textbf{124}, 229 (2002).
\textsuperscript{9} M. Valldor and M. Andersson, Solid State Sci. \textbf{4}, 923 (2002).
\textsuperscript{10} L. C. Chapon, P. G. Raduelli, H. Zheng, and J. F. Mitchell, Phys. Rev. B \textbf{74}, 172401 (2006).
\textsuperscript{11} M. Soda, Y. Yasui, T. Moyoshi, M. Sato, N. Igawa, and K. Kakurai, J. Phys. Soc. Jpn. \textbf{75}, 054707 (2006).
\textsuperscript{12} M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, H.-H. Hsieh, H.-J. Lin, C.-T. Chen, and L. H. Tjeng, Phys. Rev. Lett. \textbf{97}, 176405 (2006).
\textsuperscript{13} Z. Hu, H. Wu, M. W. Haverkort, H. H. Hsieh, H.-J. Lin, T. Lorenz, J. Baier, A. Reichl, I. Bonn, C. Felser, A. Tanaka, C. T. Chen and L. H. Tjeng, Phys. Rev. Lett. \textbf{92}, 207402 (2004).
\textsuperscript{14} M. Valldor, Solid State Sci. \textbf{6}, 251 (2004).
\textsuperscript{15} E. V. Tsipis, V. V. Kharton, J. R. Frade, and P. Núñez, J. Solid State Electrochem. \textbf{9}, 547 (2005).
\textsuperscript{16} E. V. Tsipis, D. D. Khalyavin, S. V. Shiryaev, K. S. Redkina, and P. Núñez, Mater. Chem. and Phys. \textbf{92}, 33 (2005).
\textsuperscript{17} A. Maignan, V. Caignaert, D. Pelloquin, S. Hébert, V. Praelong, J. Hejtmanek, and D. Khomskii Phys. Rev. B \textbf{74}, 165110 (2006).
\textsuperscript{18} M. Valldor, N. Hollmann, J. Hemberger, and J. A. Mydosh Phys. Rev. B \textbf{78}, 024408 (2008).
\textsuperscript{19} F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom. \textbf{67}, 529 (1994).
\textsuperscript{20} A. Tanaka and T. Jo, J. Phys. Soc. Jpn. \textbf{63}, 2788 (1994).
\textsuperscript{21} T. Burnus, Z. Hu, H. H. Hsieh, V. L. J. Joly, P. A. Joy, M. W. Haverkort, H. Wu, A. Tanaka, H.-J. Lin, C. T. Chen, and L. H. Tjeng Phys. Rev. B \textbf{77}, 125124 (2008).
22 T. Burnus, Z. Hu, H. Wu, J. C. Cezar, S. Niitaka, H. Takagi, C. F. Chang, N. B. Brookes, H.-J. Lin, L. Y. Jang, A. Tanaka, K. S. Liang, C. T. Chen, and L. H. Tjeng, Phys. Rev. B 77, 205111 (2008).

23 CoO$_4$ cluster parameters for Co$^{2+}$ [eV]: $\Delta = 6.5$, $pd\sigma = -1.53$, $U_{dd} = 6.5$, $U_{pd} = 8.2$, $10Dq = -0.15$, Slater integrals and spin-orbit coupling 70% of the Hartree-Fock values.

24 S. I. Csiszar, M. W. Haverkort, Z. Hu, A. Tanaka, H. H. Hsieh, H.-J. Lin, C. T. Chen, T. Hibma, and L. H. Tjeng, Phys. Rev. Lett. 95, 187205 (2005).

25 W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).

26 J. H. Park, PhD Thesis, University of Michigan (1994); the energy position of this FeO spectrum is recalibrated using the spectrum of an FeO thin film measured simultaneously with the Fe$_2$O$_3$ single crystal reference.

27 FeO$_4$ cluster parameters [eV]: $\Delta = 3.5$, $pd\sigma = -1.65$, $U_{dd} = 5.0$, $U_{pd} = 6.0$, $10Dq = -0.35$, Slater integrals 70% of Hartree-fock values.

28 CoO$_4$ cluster parameters for Co$^{3+}$ [eV]: $\Delta = 3.0$, $pd\sigma = -1.53$, $U_{dd} = 5.5$, $U_{pd} = 7.0$, $10Dq = -0.36$, Slater integrals 65% of Hartree-fock values.

29 C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill (1962) p. 110.