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MODELING SPIN TRANSITIONS IN LaCOO_3

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Abstract

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A novel method for simulating spin multiplets in transition metal compounds is employed to reproduce the room temperature cobalt 3s spectra for the analysis of LaCoO_3 . Particular emphasis is placed on the room temperature spectra, with a comparison between the low spin-high spin mixed final state and the intermediate spin final state as a complement to previous experimental work. [1]

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To my grandfather,

Lloyd Godfrey Mann,

font of wisdom, source of deep inspiration, war hero.

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1 Introduction

Lanthanum Cobaltite (LaCoO_3) has been of interest to the scientific community for decades because of its novel temperature-dependent electronic properties. Below 90K, the material is a nonmagnetic semiconductor, with a gradual transition to paramagnetism around 90K, where the magnetic susceptibility flattens significantly. Above 500K, the material becomes a metal [2]. The nature of these phase transitions is thought to be related to concurrent changes in the electronic spin-states. As such, much work has been done attempting to calculate the exact nature of the spin transitions with temperature.

Historically, two different theories of spin transitions have been put forward: a Low-Spin to Intermediate-Spin (LS-IS) and a Low-Spin to High-Spin (LS-HS) model. Goodenough et al. [3] initially argued in favor of a high-spin final state transition in 1967. Then, the early 1990's Korotin et al. argued strongly in favor of the LS-IS model, and subsequent experimental evidence seemed to support that theory. [4, 1, 5] However, theoretical work by Haverkort et al. [6] seemed to imply a LS-HS transition again, and experimental work by Belanger, et al. showed results inconsistent with the LS-IS model and supporting a LS-HS interpretation.. [1] Since then, there has been renewed exploration of LaCoO_3 . However, there has so far been no satisfactory LS-HS model to explain the experimental results of photoemission spectroscopy. It is the goal of this thesis to provide more experimental and theoretical evidence for either the LS-HS or IS model.

This thesis will explain the fundamentals of Core Level Photoelectron Spectroscopy, one of the primary tools used in probing electronic structures, as well as a novel model developed to

determine transition metal spin-states. After such foundation is laid, we will present the predictions this model makes for LS-HS transitions and intermediate spin approximations in the cobalt 2p and 3s orbitals in LaCoO_3 .

2 Tools and Models

It is not the intent of this thesis to provide a deep explanation of the theories or tools therein. Rather, it is very important that the reader get some idea of the foundation of various methods before any understanding of results stated later on is viable. With this in mind, we will provide some basic information pertaining to photoelectric spectra and models used in its interpretation, but leave more detailed discussion to others (especially see Hüfner's *Photoelectron Spectroscopy*[7]).

2.1 Core Level Photoemission Spectroscopy

Photoemission spectroscopy is an elegant tool developed from the assertions of photoemission. Aside from being an important early factor in the development of quantum mechanics, the quantization of light and photoemission have allowed researchers previously unprecedented tools in divining the nature of materials. Core level photoemission spectroscopy is an exploitation of the photoelectric effect to determine energy levels of electron orbitals.

Photoemission itself is a relatively simple phenomenon, wherein an electron trapped in a potential well of energy β absorbs an incident photon of some energy α . If α is less than β , the electron reradiates a photon of the same energy. However, if $\alpha > \beta$, the electron escapes confinement and now has kinetic energy $\alpha - \beta$, which can be measured. This relation is symbolically expressed by:

$$\gamma_{\alpha} + e_{\beta}^{-} \implies e_{\alpha-\beta}^{-} \quad (2.1)$$

Thus, knowing the energy of incident light (in the case of this work, from a synchrotron

radiation source such as an X-ray anode), and measuring the energy of the free electron, one can deduce quite simply the energy of the electron orbital. Of course, there are a few assumptions that must be made before such a tool is usable. These – the Sudden Approximation and the Three Step Model – are outlined in the next two subsections.

2.1.1 Sudden Approximation

The Sudden Approximation is the relatively simple assertion that once an electron is freed from an orbital, it exits the potential well of the atom quickly enough that the eigenstate of the electron decouples from that of the atom before the atomic system is able to reconfigure itself due to the new distribution of charges (minus the ejected one).

2.1.2 Three-Step Model

The three-step model is a breakdown of the photoemission process into three discrete steps:

1. An incident photon is completely absorbed by an electron in the sample, which then becomes excited.
2. The electron proceeds to travel to the surface of the sample. If it interacts with any particles along the way its energy will be lowered and can be subtracted off.
3. The electron escapes the sample and can be measured.

2.2 The Matrix Model of Gweon, Park and Oh

2.2.1 The Van Vleck Effect

John Hasbrouck van Vleck is widely credited with first quantifying multiplet splitting in solids.[8] Multiplet splitting is a result of the difference between possible angular momentum configurations (and thus total angular momentum) in the atomic final state after photoemission. The

aptly named van-Vleck theorem describes the energy difference between such configurations:

$$\Delta E = \frac{2S+1}{2l-1} G^l(s, l) \quad (2.2)$$

where S is the total spin of the pre-photoemission atom, l the valence shell, s the filled shell from which our photoelectron is excited, and $G^l(s, l)$ is known as the exchange integral.

However, like many problems in physics, such a simple model does not describe experimental results very well. There are a number of other considerations in the analysis of photoemission spectra, in the case of LaCoO_3 (and other transition-metal oxides) two notable effects are intrashell correlation and charge transfer splitting.

2.2.2 Intrashell Correlation

Bagus, Freeman, and Sasaki were the first to introduce intrashell correlation to the charge transfer model in the early 1970's.[9] In essence, after photoemission the remaining electrons are thought to distribute themselves amongst the remaining shells. Specifically, Bagus, Freeman, and Sasaki looked at the final state excitations $\underline{3s}3d^n \rightarrow \underline{3p^2}3d^{n+1}$, and $\underline{3s}3d^n \rightarrow \underline{3s3p^2}3d^{n+2}$, and put forth intrashell correlation as a way of resolving discrepancies in the energy separation and intensity ratio of peaks in spin-orbit splitting.

2.2.3 Charge Transfer Splitting

Charge transfer splitting is the result of the Coulomb interaction between the core hole and ligand. In covalent bonds (low difference in hole-ligand electronegativity) the ligand 'shares' an electron with the transition metal, and this may fill the empty d orbital of the post-emission transition-metal ion. This effect is quite visible in LaCoO_3 .

2.2.4 The Current Model

The model used in this analysis was first presented by Gweon, Park and Oh in 1993.[10] It is a charge transfer model that attempts to incorporate the core-hole screening on equal footing with

the van Vleck effect, thereby giving the researchers the ability to determine through experimental analysis the exact effect of each process in the spectroscopy of transition-metal molecules. Although this model is quite complicated it is best to first describe, as the researchers did, the more complex low-spin final state and then describe the relatively simple steps necessary to arrive at the high-spin final state or the ground state.

For the low-spin final state, the researchers considered only excitations of the type $\underline{3s}3d^n \rightarrow \underline{3p}^23d^{n+1}$ for the intrashell correlation, as other excitations did not have nearly as high a contribution. We will now describe the hamiltonian matrix for the low-spin state model, with an explanation of the variables after:

$$\langle \underline{3s}3d^n | H | \underline{3s}3d^n \rangle = E_{MHT}$$

$$\langle \underline{3s}3d^{n+1} \underline{L} | H | \underline{3s}3d^{n+1} \underline{L} \rangle = E_{MHT} + \Delta - Q_L$$

$$\langle \underline{3s}3d^{n+2} \underline{L}^2 | H | \underline{3s}3d^{n+2} \underline{L}^2 \rangle = E_{MHT} + 2(\Delta - Q_L) + U$$

$$\langle \underline{3p}^23d^{n+1} | H | \underline{3p}^23d^{n+1} \rangle = E_{MHT} + E_{ic}$$

$$\langle \underline{3p}^23d^{n+2} \underline{L} | H | \underline{3p}^23d^{n+2} \underline{L} \rangle = E_{MHT} + E_{ic} + 2(\Delta - 2Q_{3p} + u) + U$$

$$\langle \underline{3p}^23d^{n+3} \underline{L}^2 | H | \underline{3p}^23d^{n+3} \underline{L}^2 \rangle = E_{MHT} + E_{ic} + 2(\Delta - 2Q_{3p} + u) + 3U$$

$$\langle \underline{3s}3d^n | H | \underline{3s}3d^{n+1} \underline{L} \rangle = \sqrt{10 - n}T$$

$$\langle \underline{3s}3d^{n+1} \underline{L} | H | \underline{3s}3d^{n+2} \underline{L}^2 \rangle = \sqrt{2(9 - n)}T$$

$$\langle \underline{3s}3d^{n+2} \underline{L}^2 | H | \underline{3s}3d^{n+3} \underline{L}^3 \rangle = \sqrt{3(8 - n)}T$$

$$\langle \underline{3p}^33d^{n+1} | H | \underline{3p}^33d^{n+2} \underline{L} \rangle = \sqrt{(9 - n)}T$$

$$\langle \underline{3p}^23d^{n+2} \underline{L} | H | \underline{3p}^23d^{n+3} \underline{L}^2 \rangle = \sqrt{2(8 - n)}T$$

$$\langle \underline{3s}3d^{n+q} \underline{L}^q | H | \underline{3p}^23d^{n+q+1} \underline{L}^q \rangle = V_{ic}$$

Where E_{MHT} is the energy separation predicted by multiplet-hole theory, Δ is the charge-transfer energy, Q_L and Q_{3p} are the Coulomb interaction between the core hole and the d electron

for the low-spin state and 3p orbital, respectively. U is the $d-d$ Coulomb interaction, u is the d electron-ligand hole Coulomb interaction, T is a hopping parameter between the ligand p orbital and the transition-metal d orbital, and E_{ic} and V_{ic} are new parameters representing the energy separation and coupling strength due to the intrashell correlation effect respectively.

Setting E_{ic} and V_{ic} to zero gives the high-spin final state, and we should expect parameters that describe valence band structure (Δ, u, U , and T) to be the same, whereas Q should be quite different and is denoted by Q_H . It is important to note that these Q values correspond to the final state of the photoemission process – they have nothing to do with the initial high, low, or intermediate spin states whose nature we are trying to deduce. The ground state can be summarily found by setting $Q_H = 0$. Analysis and interpretation of the Hamiltonian is as follows:

“The energy of positions of various photoemission peaks are given by the eigenvalues of the final-state Hamiltonian, and their intensities are given by the overlap between the final eigenstate and the lowest initial eigenstate by the sudden approximation.” [10]

3 Experiment and Analysis

The spectra for this paper were produced by Gey-hong Gweon at Beamline 7 of the Advance Light Source at Lawrence Berkeley Labs in Berkeley, California. An initial issue in our consideration is the fact that the Lanthanum $4d$ orbital overlaps that of the $Co3s$. Thus, the spectra were taken at room temperature with the overlapping $La4d$ spectrum subtracted off in differing amounts. These spectra are shown in Fig. 3.1, where the red line is the raw data, the blue line has had the maximum $La4d$ intensity subtracted off by half, and the maximum $La4d$ intensity has been subtracted completely off the green line. It is our belief that the 'true' $Co 3d$ line lies somewhere between these last two.

3.1 The $2p$ Spectra

Saitoh et al. [2] produced photoemission spectra of the cobalt $2p$ orbital in 1997. This work is widely regarded as well done, and so our first step was to produce a fit using our new model. Figure 3.2 is a reproduction of their spectrum with our best estimate overlaid.

If we could reproduce the well-researched $2p$ spectra and obtain parameters similar in value to previous work [11], we would be justified in using our model to interpret the $3s$ spectra. As can be seen, there is good agreement between data and theory for the large scale effects. However, there is significant disagreement in the area between the main and spin-orbit peaks (the largest and second largest, respectively), as well as a slightly higher energy than predicted to the left of the spin-orbit peak. It is to be expected that a rough model such as ours would not completely

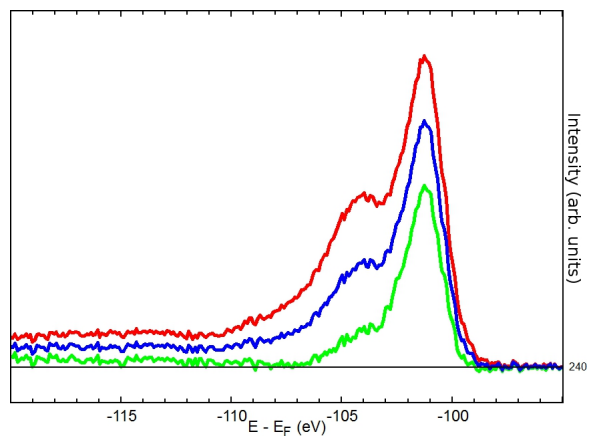


Figure 3.1: The three spectra evaluated in this paper with various intensities of the $\text{La}4d$ spectra subtracted off.

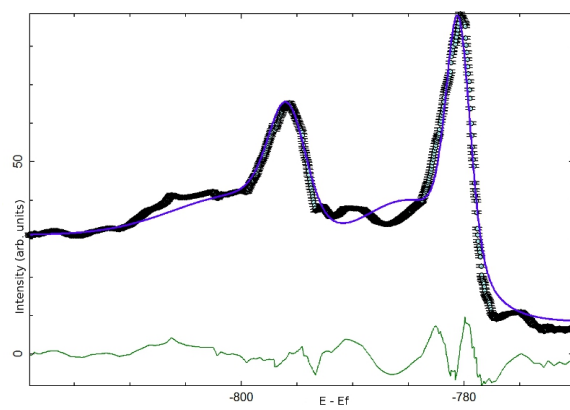


Figure 3.2: The 2p spectra for Lanthanum Cobaltite with a best-fit line.

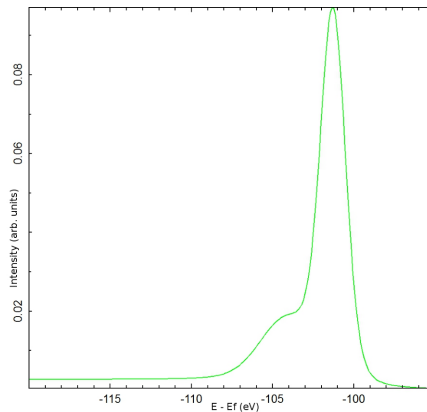


Figure 3.3: The 3s low-spin initial state.

reproduce photoemission spectra, and the values of Q_{2p} , Δ , u , U , and E_{MHT} are all in agreement with previous work, and so we decided to take the atomic values (Δ , u , U , T) and extend them to the 3s spectra.

3.2 The 3s Spectra

As stated previously, our first step in analyzing the 3s spectra was to simply produce low-, intermediate-, and high-spin lines from the atomic data found in the 2p analysis. Figures 3.3, 3.4, and 3.5 are these productions, respectively.

Haverkort et al. [6] produced a curve describing temperature-based LS-HS mixing ratios, from which we have based our analysis. Following is a discussion of the room temperature spectra with varying amounts of the La4d spectrum subtracted off.

3.2.1 The Raw Data Minus the Maximum possible contribution of the La4d orbital

The green line in Fig. 3.1 is the 3s spectrum with no possible contribution from the La4d spectrum. Visual analysis shows the highest ratio of main peak to charge-transfer peak, and the

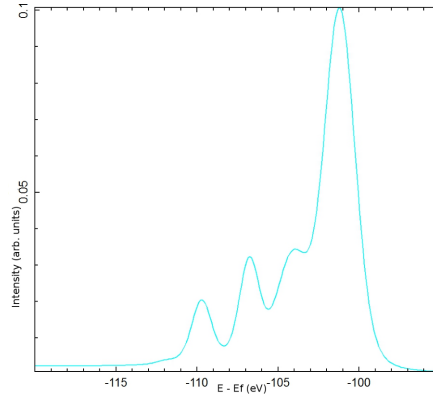


Figure 3.4: The 3s intermediate-spin approximation.

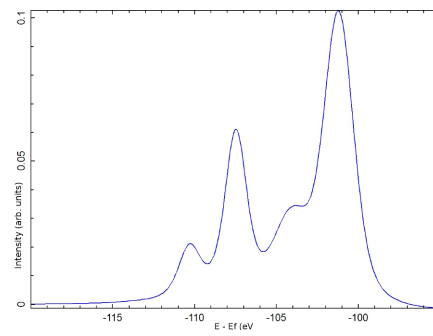


Figure 3.5: The 3s high-spin initial state.

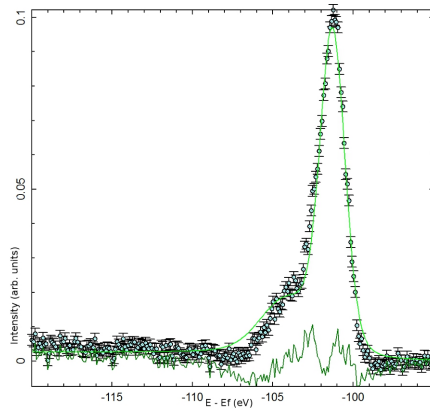


Figure 3.6: A low-spin reproduction of the line with no possible La4*d* contribution.

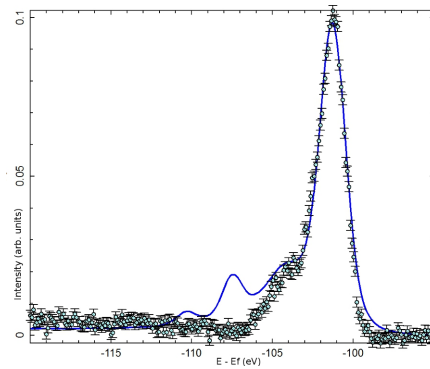


Figure 3.7: A low spin-high spin reproduction of the line with no possible La4*d* contribution.

Haverkort paper posits an initial high-spin state mixture between 20 and 30 percent. Fig. 3.6 shows the LS approximation of this line, and fig. 3.7 is the LS-HS approximation with a 25% HS mixing ratio.

The mixed-spin model is clearly a good approximation and can become better with some simple adjustments (clearly, it is also possible to satisfactorily emulate this temperature regime using acceptable atomic values with only the LS initial state, but that does not hold for the other lineshapes). As a comparison, Fig. 3.8 shows the IS approximation of this spectrum. The main peak is (as expected) still well represented, and the charge transfer peak has the correct difference

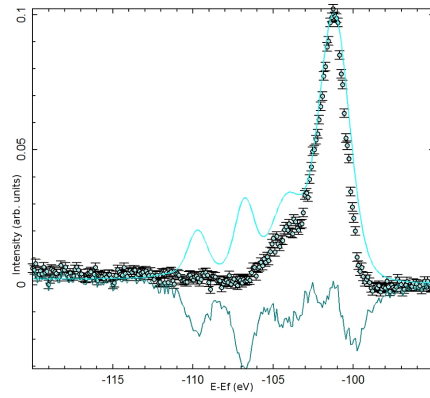


Figure 3.8: The intermediate-spin approximation for the line with no possible La4d contribution.

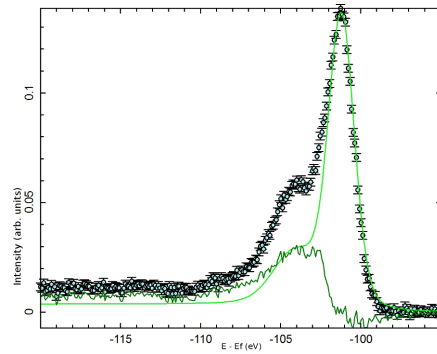


Figure 3.9: The low spin approximation. Note the significant disagreement in intensity of the charge transfer peak.

in electron-volts. However, it would be quite difficult to correct the lower energy peaks without changing atomic variables to significantly outside the physical regimen.

3.2.2 The 3s Line with half the maximum La4d Contribution

Figs. 3.9, 3.10, and 3.11 are the LS, LS-HS, and IS approximations for this line.

The intermediate spin approximation clearly agrees with the main features of this line the most. However, the exchange-splitting contribution is much higher than for the LS-HS case, and this is clearly not present in the data. On top of this, it is at present not known how much the La4d line contributes to these spectra, and so it is not possible to obtain the exact 3s spectral line. We

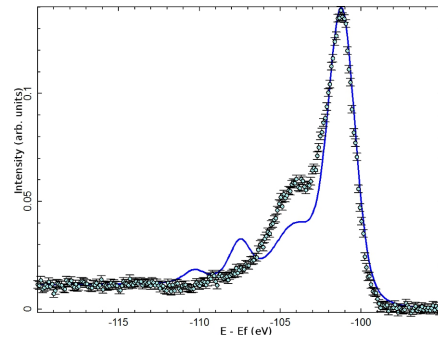


Figure 3.10: The low spin-high spin reproduction. There is significantly less disagreement than the LS case.

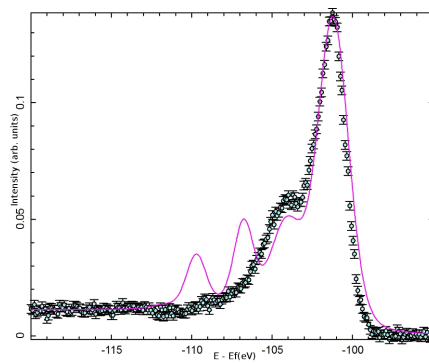


Figure 3.11: The intermediate spin reproduction. Note the very close agreement for the main and charge-transfer peaks, and the significant contribution of the exchange-splitting peaks that is not present in the data.

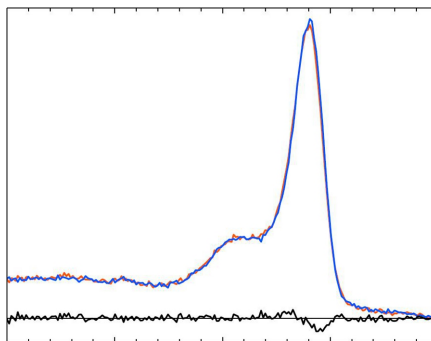


Figure 3.12: An illustration of the temperature dependence of the $3s$ spectrum. The red line is 500 kelvin, and the blue is 300K. (Thanks to Gey-Hong Gweon for the use of this image)

believe the true line to lie somewhere between these previous two spectra, and once it is determined we can truly compare the LS-HS and IS cases.

3.2.3 The Raw Data

The raw data (with the full $La4d$ contribution) are described by the red line in Fig. 3.1. We show this to give an idea of the difficulty in extracting the pure Co $3s$ orbital.

3.2.4 Spectra at Different Temperatures

Fig. 3.12 describes the temperature dependence of the Co $3s$ photoemission spectra above room temperature. Note the miniscule (almost non-existent) change. This is in striking contradiction to the theoretically produced LS-HS spectra (figs. 3.13 and 3.14), which show marked growth in the charge-transfer peak, as well as an increase in the proportion of the exchange-split peaks. These spectra then are inconsistent with the findings of Haverkort et al.[6] which posit an increase in the proportion of the HS initial state with respect to temperature. It is thus quite clear that a better theory of $3s$ photemission is required before we can have significant agreement with our data. Specifically, we require a better treatment of the mixing ratios with temperature and a universally better theory of exchange-splitting that does not dominate as much as the current one.

The molecular and electronic values used in the generation of these spectra are reproduced

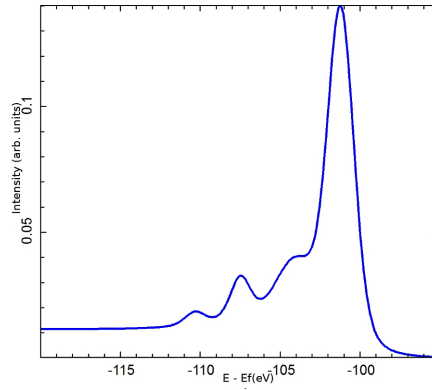


Figure 3.13: A LS-HS reproduction using a 25% HS ratio in line with Haverkort's room temperature approximation.

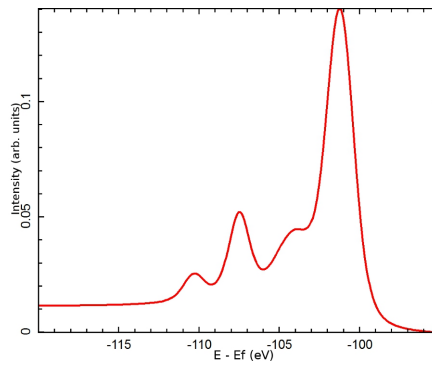


Figure 3.14: A LS-HS reproduction using a 50% HS ratio in line with Haverkort's 500k approximation.

in Table 1.

	U	T	Ti	Q_{2p}	Q_{3sH}	Q_{3sL}	Q_{3p}	u	E_{ic}	V_{ic}	E_{MHT}	Δ
2p	3.4	0.8	0.8	6.3	N/A	N/A	N/A	1.1	12.4	10.8	15	5.5
3s (low)	3.4	0.8	1.15	N/A	5.2	5.2	6	1.1	12.4	10.8	15	5.5
3s (int)	3.4	0.8	1.15	N/A	5.2	5.2	6	1.1	12.4	10.8	15	5.5
3s (high)	3.4	0.8	1.15	N/A	5.2	5.2	6	1.1	N/A	N/A	15	5.5

Table 3.1: The molecular and electronic parameters used in generating the spectra.

4 Conclusion

4.1 Next Steps

Clearly, the LS-HS and IS models do not capture the shape of these spectra as it stands. While we seem to have a good grasp of the high-spin final state main and charge-transfer peaks, the exchange splitting peaks for both models are far too large. We must find, in our models, some way to approximate this. Once that is accomplished developing appropriate fits for our data will be relatively simple; we have most of the parameters which describe the main characteristics of the spectra to within 20%, and this will certainly get better with time. When these two things are done, we should have a good understanding of the 3s Cobalt spectra in LaCoO_3 – a significant step in our understanding of this novel material.

4.2 Final Words

Our exploration of transition-metal oxides is still in its infancy; it is only with the advent and proliferation of computers that we have become finally able to perform the immense calculations required in the simulation of these materials. Like the development of any theory this one has gone and will go through many revisions before it will have any predictive capacity, but the completion of this research will yield crucial information on the effect of core-hole screening as well as hopefully giving clear theoretical evidence for either the LS-HS or the IS transition model.

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