PHILOSOPHICAL MAGAZINE B, 1999, VOL. 79, NO. 1, 1–8

Photoemission from $YbInCu_4$: testing the single impurity model

J. J. JOYCE, A. J. ARKO, J. L. SARRAO, K. S. GRAHAM

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Z. FISK

National High Magnetic Field Laboratory and Florida State University, Tallahassee, FL 32306, USA

and P. S. RISEBOROUGH

Polytechnic Institute of New York, New York, NY 11201, USA

[*Received 14 July 1998 and accepted 17 July 1998*]

ABSTRACT

The electronic properties of single crystal $YbInCu_4$ and $YbAgCu_4$ have been investigated by means of high resolution photoelectron spectroscopy. A first order, isostructural phase transition for $YbInCu_4$ at 42 K leads to changes in the Kondo temperature, of more than an order of magnitude. This phase transition and accompanying Kondo temperature change provide the most direct test of the single impurity model to date. The photoemission results are incongruous with the single impurity model predictions for temperature dependence, binding energy and 4f occupancy, encouraging a re-evaluation of the single impurity model applicability.

The electronic properties of heavy fermions have generally been explained (Allen *et al.* 1986, Patthey *et al.* 1990, Tjeng *et al.* 1993, 1994, Weibel *et al.* 1993) within the framework of the single impurity model (SIM). Particle–hole symmetry allows the SIM to be used for Yb compounds as well as Ce heavy fermions with the great advantage that the predicted Kondo resonance is found on the occupied side of the spectral weight function for Yb materials and is thus directly observable in photoemission. $YbInCu_4$ provides the finest opportunity to date for testing the predictions of the SIM. $YbInCu_4$ has an isostructural first order phase transition at $T_V = 42$ K with a 0.5% volume reduction (Sarrao *et al.* 1996) and within the SIM framework predicted changes in the electronic structure as the Kondo or characteristic temperature (T_K) changes from ~ 400 K below T_V to ~ 25 K above T_V. We report the first single crystal photoelectron spectroscopy (PES) results as they pertain to electronic properties of $YbInCu_4$ and also $YbAgCu_4$ ($T_K \approx 100$ K). In addition, we have calculated spectral weight functions using the non-crossing approximation (NCA) (Bickers *et al.* 1987) and Gunnarsson–Schönhammer (GS) (1983, 1985) methods within the SIM formalism. Examination of the experimental data and the model calculations leads to the conclusion that the SIM does not accurately represent the spectral function and hence, electronic structure of these Yb heavy fermions.

Within the framework of the SIM, a given heavy fermion has a particular characteristic temperature which describes the magnitude and temperature dependence of the interaction (Bickers *et al.* 1987, Gunnarsson and Schönhammer 1983, 1985) between the localized f electron and a spin-compensating cloud of conduction electrons. The so-called Kondo resonance then, formed by the f electron and compensating cloud, is predicted to result in a very narrow, highly temperature dependent peak in the immediate vicinity of the Fermi level. Specifically, from GS and the NCA, the Kondo resonance is at an energy proportional to $k_B T_K$ below the Fermi level (in Yb materials) with a full width at half maximum of $k_B T_K$. The NCA also predicts the temperature evolution of the spectral weight function where the spectral intensity can change by an order of magnitude (Bickers *et al.* 1987) going from well below T_K to well above T_K for a given material. $YbInCu_4$ is ideal for testing this model prediction since measurements at 20 K (below T_V) are for the high T_K phase with $T/T_K \approx 1/20$, whereas the 80 K measurements (above T_V) are for the low T_V phase with $T/T_K \approx 3$. The isostructural $YbAgCu_4$ is used as a control point showing the temperature evolution between 20 K and 80 K in a material without the phase transformation. The NCA and GS calculations can be complicated by spin–orbit and crystal field sidebands (Joyce and Arko 1993) to the Kondo resonance. Fortunately, the spin–orbit splitting (SOS) for Yb is large (1.29 eV) and is energetically removed from the Fermi level (E_F). Also, for both $YbInCu_4$ and $YbAgCu_4$ neutron scattering data indicates no crystal fields to complicate the interpretation†. Moreover, the surface contribution to the 4f spectral intensity is easily separated from the bulk contributions‡. Then, the large SOS in Yb and the lack of crystal field levels in these materials combined with the immense advantage of the isostructural phase transition for $YbInCu_4$ giving rise to a huge change in T_K (400 K to 25 K) over a narrow temperature interval with all other parameters relevant to the Kondo resonance remaining constant, provide the best test of SIM to date.

The photoemission experiments were conducted at the Synchrotron Radiation Center using the PGM undulator and 4 m NIM beamlines. The analyser was a VSW HA50 modified for multichannel detection and a changeable entrance aperture with $a \pm 1°$ or $\pm 4°$ angular acceptance. The crystal structure for $YbXCu_4$ (X = In, Ag) is cubic (C15b) with a lattice constant of 7.15 Å for $YbInCu_4$. The photoelectron spectra were taken at two photon energies. The PES data taken at a photon energy of 40 eV, an energy resolution of 45 meV, and the $\pm 4°$ aperture sampled $\sim 50\%$ of the sample Brillouin zone. The PES data taken at a photon energy of 90 eV, an energy resolution of 85 meV, and the $\pm 1°$ aperture sampled $\sim 20\%$ of the sample Brillouin zone. No angle-resolved effects were observed in the spectra of the bulk Yb 4f levels. Energy resolution was determined by means of the gold Fermi level. The measurement temperatures were 20 K and 80 K, set by using a flow-through cryostat with liquid nitrogen or liquid helium. The single crystal samples were grown by the

† The neutron data for $YbAgCu_4$ are unambiguous, however, the results on $YbInCu_4$ are not as universally accepted. It is possible that crystal field levels exist 3.2 and 3.8 meV below a Γ_8 ground state (Severing *et al.* 1990) but these states would be close enough to T_K, in any event, so as not to appreciably alter the calculations.

‡ Details of the 4f component designations as well as lineshape analysis, background and non-f intensity removal are specified in Joyce *et al.* (1996) and to a lesser extent in Joyce *et al.* (1994) and Joyce and Arko (1997).

flux growth method (Sarrao *et al.* 1996) and the sample surface was prepared *in situ* by post cleaving the samples along a high symmetry axis in a vacuum of 7×10^{-11} Torr.

We test directly three of the central predictions of the SIM; the temperature dependence of the Kondo resonance spectral intensity, the 4f hole occupancy, and the energy shift of the Kondo resonance as a function of T_K. These three SIM predictions are tested against PES measurements for $YbInCu_4$ and $YbAgCu_4$. In

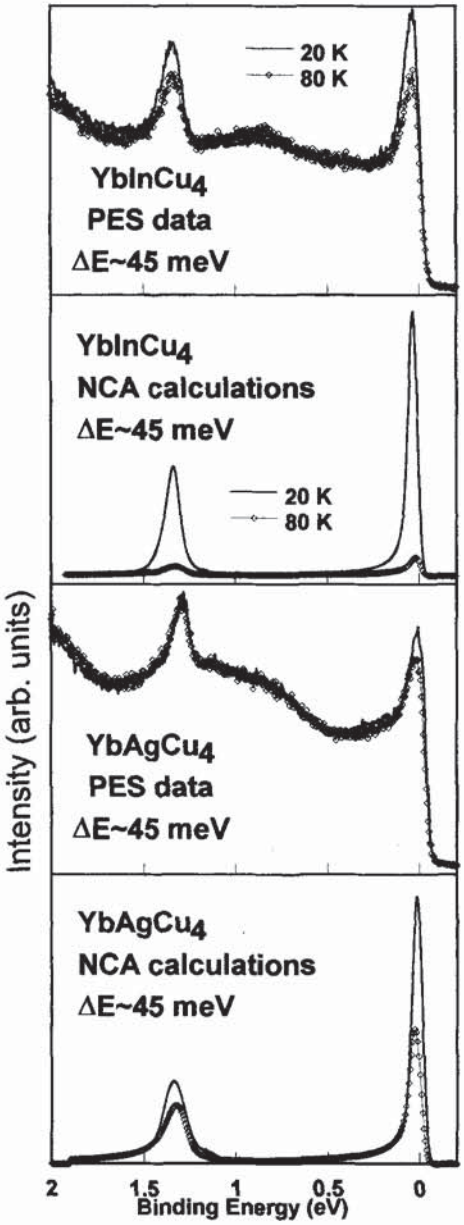

Figure 1. PES data at $h\nu = 40$ eV and NCA calculations for $YbInCu_4$ and $YbAgCu_4$. The calculations have been convoluted with the appropriate Fermi function and broadened by the experimental resolution of 45 meV.

figure 1 we show the PES data at two temperatures followed by the NCA calculations for the same material at the same two temperatures. The experimental resolution was 45 meV at a photon energy of 40 eV and the NCA calculations have been broadened by this same amount and cut by the appropriate Fermi function to facilitate comparison with the PES results. The top two frames of figure 1 show the results for $YbInCu_4$ at 20 K and 80 K, bracketing the phase transition at 42 K. The 4f related features in the valence band are identified as the bulk $4f_{7/2}$, surface $4f_{7/2}$ and the bulk $4f_{5/2}$ moving away from the Fermi level with binding energies of 0.02 eV, 0.85 eV and 1.3 eV respectively. For the PES data, the change in the integrated spectral intensity for the bulk 4f features of Yb in $YbInCu_4$ is about 25% between 20 and 80 K. The SIM model calculations using the NCA framework for the same material and temperature range show a reduction in the 4f spectral intensity by a factor of 10. Comparisons between the SIM calculations and the PES data strongly indicate problems with the model predictions.

The lower two frames of figure 1 show the PES data taken at 40 eV and NCA predictions for $YbAgCu_4$. This material is isostructural with $YbInCu_4$ but does not show a volume collapse phase transition. Here the NCA calculations at both temperatures are for $T_K \approx 100$ K. Now the PES data show less than 5% intensity loss between 20 an 80 K while the NCA predicts a 35% loss in intensity. Again the PES data and the SIM calculations are at odds indicating a serious problem with the application of SIM to these Yb heavy fermions. The following parameters were used for the $YbInCu_4$ NCA calculations to arrive at the above specified T_K values, conduction band width 6 eV; bare f level -1.0 eV, SOS 1.29 eV; crystal field levels–none; hybridization (Δ) = 0.067 37 eV for $T_K \approx 400$, and $\Delta = 0.046\,33$ eV for $T_K \approx 25$ K, with the same parameters used for $YbAgCu_4$ but with Δ adjusted to yield $T_K \approx 100$ K. Slightly different values of Δ were used in the GS calculations with the T_K, SOS, bare f and conduction band widths held fixed at the NCA values. The differences required in the Δ values between the two calculations to maintain the same T_K values arise from the difference in the conduction band lineshape. The NCA calculations use a Lorentzian conduction band while the GS calculations use a flat conduction band.

We examine the SIM prediction of a binding energy shift going from $T_K \approx 400$ K to $T_K \approx 25$ K. It has previously been demonstrated that the binding energy of the $4f_{7/2}$ level in $YbAgCu_4$ is inconsistent with a SIM interpretation (Weibel *et al.* 1993, Joyce *et al.* 1996) but in $YbInCu_4$ one can actually look for changes in binding energy rather than absolute values. A comparison between GS calculations (top frame) and the PES data at $h\nu = 40$ eV for $YbInCu_4$ (bottom frame) on either side of the T_V phase transition are presented in figure 2. As an aside, the inset in figure 2 shows a comparison of the NCA and GS calculations for $YbInCu_4$ in the region of the $4f_{7/2}$ emission. The two SIM calculations are essentially the same within the experimental resolution of the present study so that the SIM models are indeed self consistent; they are not, however, necessarily (or in fact) correct. Figure 2 presents PES data and GS calculations for the SOS component ($4f_{5/2}$) of the Yb 4f emission. The SOS of the 4f manifold does not depend on T_K (so the $4f_{5/2}$ level like the $4f_{7/2}$ level should show a binding energy directly dependent on T_K) and since the $4f_{7/2}$ level is energetically very near the Fermi level (~ 25 meV from E_F by lineshape analysis) the shift in this spectroscopic feature could possibly be masked to some extent, by the role of the Fermi function whereas the $4f_{5/2}$ level is unaffected by E_F. Figure 1 demonstrated the extreme change in predicted NCA intensity as a

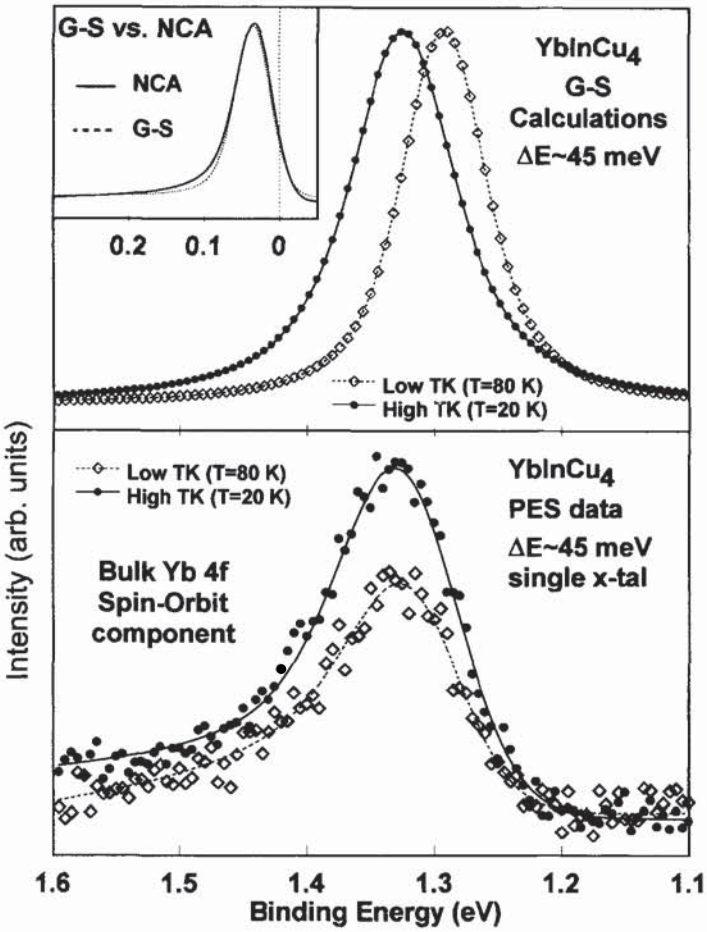

Figure 2. GS calculations and PES data at $h\nu = 40$ eV for $YbInCu_4$ in the region of the spin–orbit split component for the Yb 4f bulk divalent signal. The top frame shows the GS calculation for the different T_K above and below T_V. The inset to the top frame shows a comparison between NCA and GS calculation for the same material. The lower frame shows the PES results for the Yb $4f_{5/2}$ level at temperatures above and below T_V. All calculations have been broadened for the experimental resolution of 45 meV. The SIM predicted shift in the binding energy is absent from the PES data.

function of temperature. We have now normalized the GS calculations (after broadening by the experimental resolution) in figure 2 to be of the same amplitude in order to examine the details of the predicted energy shift. The GS calculations (top of figure 2) predict a 33 meV shift in the peak position of the Yb $4f_{5/2}$ as well as the $4f_{7/2}$ level in $YbInCu_4$. The PES data (bottom of figure 2) for $YbInCu_4$ however, show no such energy shift which would be trivially observed at the stated experimental resolution. Once again fundamental SIM predictions are not observed in the PES data.

There remain discrepancies in the reported PES results for Yb heavy fermion systems. In general, the discrepancies arise between measurements on cleaved single crystal samples and polycrystalline samples with varying surface preparation methods. In particular, the differences between single crystal and polycrystal samples have

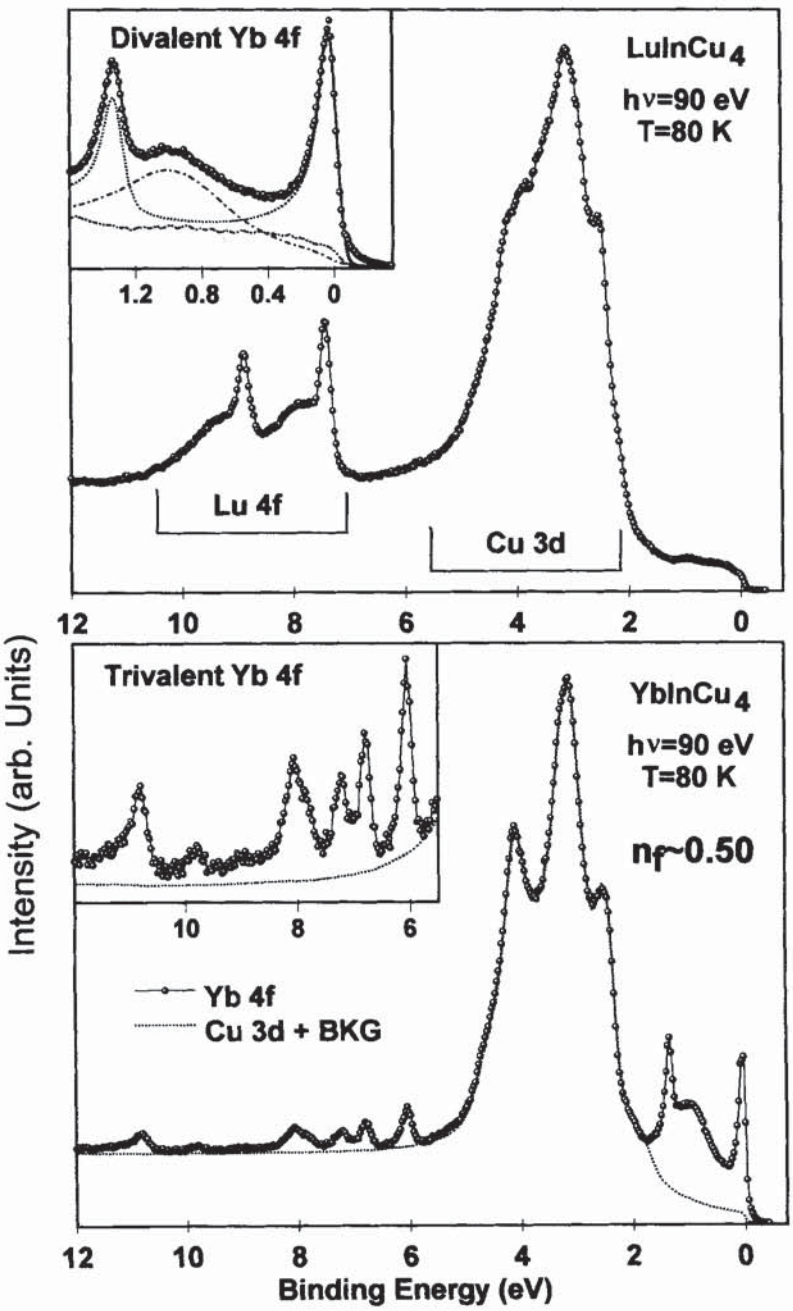

Figure 3. Photoemission data for $LuInCu_4$ and $YbInCu_4$ at 80 K with $YbInCu_4$ in the low T_K ($\sim$ 25 K) phase. The top frame shows $LuInCu_4$ as a reference spectrum to indicate the non-4f contributions to the spectral weight at 90 eV and indicates the region of the Cu 3d and the Lu 4f emission. The inset to the top frame shows the lineshape analysis for the divalent Yb 4f region with separations into surface (dot) and bulk (dot, dash) as well as the Lu contribution (dot, dot, dash) near e_F. The lower frame shows $YbInCu_4$ measured at 80 K and 90 eV photon energy. The trivalent 4f emission has been isolated in the inset to show the structure of the fractional parentage for the $4f^{13} \rightarrow 4f^2$ emission. The divalent emission is within the first 2 eV of the Fermi level.

been addressed for $YbAl_3$ (Joyce *et al.* 1994), YbB_{12} (Joyce and Arko 1997), and now for $YbInCu_4$ (Okusawa *et al* 1996). A general discussion of these differences can be found in appendix B of Joyce *et al.* (1996). In the case of $YbInCu_4$, the quality of the samples can be further confirmed by the sharpness of the T_V transition as indicated in Sarrao *et al.* (1996) and we proceed from the assessment that the confidence level for these experimental results are high for the single crystal samples.

The discrepancies between SIM and experimental data persist with SIM predicting a hole occupancy (n_f) for the low T_K phase of $YbInCu_4$ in the range of 0.9 to 0.95 (Cornelius *et al.* 1997) while PES determines the n_f to be 0.5, much closer to the values used in a band calculation (Takegahara and Kasuya 1990) for $YbInCu_4$. Our PES measurements also indicate a $\Delta n_f \approx 0.11$ between the two phases of $YbInCu_4$. The hole occupancy is defined as $n_f = I(f^{13})/[I(f^{13}) + \frac{13}{14} I(f^{14}_{bulk})]$, where $I(f^{13})$ is the integrated intensity of the primary trivalent 4f component and $I(f^{14}_{bulk})$ is the integrated primary bulk divalent 4f component from the lineshape analysis. The full valence band spectra for $YbInCu_4$ and $LuInCu_4$ taken at a photon energy of 90 eV are shown in figure 3. The top frame of figure 3 shows $LuInCu_4$ which is used to determine the non-4f contribution to the emission in the vicinity of the Yb divalent 4f spectral weight while the inset to the top frame shows the fitting of the divalent $YbInCu_4$ region. The lineshape analysis discussed in Joyce *et al.* (1996) is used to separate the 4f from the non-4f as well as the 4f divalent signal into surface and bulk components. The bottom frame of figure 3 shows the full valence band spectrum for $YbInCu_4$ at 80 K with the dashed line showing the inelastic background electron emission along with the Cu 3d states. The region of the Yb 4f trivalent emission is enlarged in the inset between 12 and 6 eV. By isolating the primary emissions in this manner, for both the trivalent and bulk divalent 4f signals, we are able to calculate the n_f for the 4f levels. The PES data gives an $n_f = 0.50$ for $YbInCu_4$ at $= 80$ K which is well above T_V and thus places the material in the low T_K phase where SIM predicts $n_f > 0.90$.

In summary, $YbInCu_4$ with its isostructural phase transition provides the best test to date of the applicability of the SIM to Yb-based heavy fermions. In light of the SIM discrepancies compared with the experimentally measured PES values including binding energy shifts, temperature dependence and n_f values, it would seem prudent to investigate other avenues of interpretation for heavy fermion characteristics beyond the SIM. This finding is consistent with fundamental questions raised recently regarding the applicability of SIM (Arko *et al.* 1997a, b, c) to Ce and U correlated electron systems. The observation of f-electron dispersion in Ce and U compounds both above and below T_K leads one to consider new models (Jarrell 1995, Sheng and Cooper 1995, Liu 1997) which incorporate both lattice effects and electron correlations but can also address, at least qualitatively, the issues of dispersion in Ce and U as well as the greatly reduced temperature dependence and lack of T_K scaling found in Yb heavy fermions.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the US Department of Energy. The Synchrotron Radiation Center is operated by the University of Wisconsin for the National Science Foundation under award #DMR-95-31009. J. L. S. and Z. F. acknowledge support from the NSF through grant #DMR-9501529 and through cooperative agreement #DMR-9016241. We are very grateful for the NCA source codes which were written and provided by M. Makivic and D. L. Cox.

References

Allen, J. W., Oh, S.-J., Gunnarson, O., Schonhammer, K., Maple, M. B., Torikachvili, M. S., and Lindau, I., 1986, *Adv. Phys.*, **35**, 275.

Arko, A. J., Joyce, J. J., Andrews, A. B., Mandrus, D., Moshopoulou, E., Fisk, Z., and Canfield, P. C., 1997a. *Phil. Mag.* B, **75**, 603.

Arko, A. J., Joyce, J. J., Andrews, A. B., Thompson, J. D., Smith, J. L., Mandrus, D., Hundley, M. F., Cornelius, A. L., Moshopoulou, E., Fisk, Z., Canfield, P. C., and Menovsky, A. A., 1997b, *Phys. Rev.* B, **56**, R7041.

Arko, A. J., Joyce, J. J., Andrews, A. B., Thompson, J. D., Smith, J. L., Moshopoulou, E., Fisk, Z., Menovsky, A. A., Canfield, P., and Olson, C. G., 1997c, *Physica* B, **230–232**, 16.

Bickers, N. E., Cox, D. L., and Wilkins, J. W., 1987, *Phys. Rev.* B, **36**, 2036.

Cornelius, A. L., Lawrence, J. M., Sarrao, J. L., Fisk, Z., Hundley, M. F., Kwei, G. H., Thompson, J. D., Booth, C. H., and Bridges, F., 1997, *Phys. Rev.* B, **56**, 7993.

Gunnarsson, O., and Schönhammer, K., 1983, *Phys. Rev.* B, **28**, 4315; 1985, *Phys. rev.* B, **31**, 4815.

Jarrell, M., 1995, *Phys. Rev.* B, **51**, 7429 (private communication).

Joyce, J. J., Andrews, A. B., Arko, A. J., Blyth, R. I. R., Bartlett, R. J., Olson, C. G., Poirier, D. M., Canfield, P. C., and Benning, P., 1996, *Phys. Rev.* B, **54**, 17515.

Joyce, J. J., and Arko, A., 1993, *Phys. Rev. Lett.*, **70**, 1181; 1997, *Phys. Rev. Lett.*, **78**, 1831.

Joyce, J. J., Arko, A. J., Andrews, A. B., and Blyth, R. I. R., 1994, *Phys. Rev. Lett.*, **72**, 1774.

Liu, S. H., 1997, *Physica* B, **240**, 49.

Okusawa, M., Weschke, E., Meier, R., Kaindl, G., Ishii, T., Sato, N., and Komatsubara, T., 1996, *J. Electron. Spectros. Rel. Phenom.*, **78**, 139.

Patthey, F., Imer, J.-M., Schneider, W.-D., Beck, H., and Baer, Y., 1990, *Phys. Rev.* B, **42**, 8864.

Sarrao, J. L., Immer, C. D., Benton, C. L., Fisk, Z., Lawrence, J. M., Mandrus, D., and Thompson, J. D., 1996, *Phys. Rev.* B, **54**, 12207.

Severing, A., Gratz, E., Rainford, B. D., and Yoshimura, K., 1990, *Physica* B, **163**, 409.

Sheng, Q. G., and Cooper, B. R., 1995, *Phys. Rev. Lett.*, **78**, 123.

Takegahara, K., and Kasuya, T., 1990, *J. Phys. Soc. Jpn.*, **59**. 3299.

Tjeng, L. H., Oh, S.-J., Chen, C. T., Allen, J. W., and Cox, D. L., 1994, *Phys. Rev. Lett.*, **72**, 1775.

Tjeng, L. H., Oh, S.-J., Cho, E.-J., Lin, H.-J., Chen, C. T., Gweon, G.-W., Park, J.-H., Allen, J. W., Suzuki, T., Makivic, M. S., and Cox, D. L., 1993, *Phys. Rev. Lett.*, **71**, 1419.

Weibel, P., Grioni, M., Malterre, D., Dardel, B., Baer, Y., and Besnus, M., 1993, *Z. Phys.* B, **91**, 337.