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HALL EFFECT IN YbXCu_4 AND THE ROLE OF CARRIER DENSITY IN THE YbInCu_4 VALENCE TRANSITION

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An unrealistically large value of the Gruneisen parameter is required to explain the valence transition which occurs at 42 K in YbInCu_4 as due to a Kondo Volume Collapse. A hint as to the origin of the transition lies in the large change in carrier density which occurs at the transition, from trivalent semimetallic behavior at high temperature to mixed valent metallic behavior at low temperature. In this paper we report measurements of the Hall coefficient R_H for temperatures in the range 15–300 K for a series of RXCu_4 compounds ($\text{R} = \text{Yb, Lu}$ and $\text{X} = \text{Au, Zn, Cd, Mg, Tl}$) that form in the cubic $C15b$ structure. For all X the Hall coefficients are small ($\sim 10^{-10} \text{ m}^3/\text{C}$) so that the transport appears to be metallic. The observation that low carrier density is unique to RInCu_4 leads us to hypothesize that the valence transition (which is also unique to YbInCu_4) is connected with the existence of a quasigap, which is a common feature of the band structure of RXCu_4 . The quasigap allows for two competing hybridization states of the $4f$ electrons: a small T_K semimetallic state and a large T_K metallic state.
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1. INTRODUCTION

YbInCu_4 has a phase transition at $T_c = 42 \text{ K}$ [1–3] at which the Yb, which is nearly trivalent at high temperature, becomes strongly mixed valent ($z = 2.8$) at low temperature [1, 4]. The Kondo energy, which is small ($T_{K^+} \approx 25 \text{ K}$) at high temperature, becomes large ($T_{K^-} \approx 500 \text{ K}$) [4–6] in the low temperature state. Furthermore there is no change in the $C15b$ crystal symmetry at the transition [7, 8]. Such an “isomorphic” valence transition is fundamentally similar to the α – γ transition in cerium [9, 10], which raises the question whether both transitions have a common origin.

In the prevailing Kondo Volume Collapse (KVC) Model [10] for the Ce α – γ transition the large change in cell volume at the transition ($\Delta V/V_0 \approx 0.2$) causes the Kondo temperature to increase from a value $T_{K^+} \sim 100$ –200 K in the high temperature (γ) phase to a value $T_{K^-} \sim 1000$ –2000 K in the low temperature (α) phase. The system gains Kondo condensation energy of order kT_{K^-} at low temperature, but when the temperature becomes greater than T_{K^+} the system lowers the free energy by converting to the smaller Kondo temperature and taking advantage of the $R \ln(2J+1)$ spin entropy ($J = 5/2$ for Ce) which is liberated for $T > T_{K^+}$. This scenario depends not only on the very large (20%) volume change but also on the sensitivity of the Kondo temperature to changes in the cell volume; quantitatively it requires a value of order 50 for the Gruneisen parameter $\Gamma = -\partial \ln T_K / \partial \ln V$. Such large values of Γ are typical of heavy fermion and mixed valent compounds [11]. For γ -cerium Γ has been estimated [12] to be 25

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from the rate of change of the Curie–Weiss susceptibility parameter θ with volume; this estimate assumes the relation, valid for the Kondo effect, that $\theta \propto T_K$. For the reasons given above (and as is seen experimentally [12]) $T_c \approx T_K$ so that Γ can also be estimated from the slope of the α – γ phase boundary $(1/T_c)\partial T_c/\partial P = 2.5/\text{kbar}$; given the bulk modulus $B = 200 \text{ kbar}$ [13] this implies $\Gamma = 50$.

The valence transition in YbInCu₄ also can be viewed as a competition between a low temperature state with a large Kondo condensation energy and a high temperature state with a large spin entropy ($J = 7/2$ for Yb). However, the change in cell volume at the valence transition in YbInCu₄ is so small ($\Delta V/V_0 \approx 0.005$) [3, 5, 8] that to drive a change in T_K from 25 K to 500 K would require an unphysically large value (~ 4000) of the Grüneisen parameter. Since it has been determined experimentally [4] for YbInCu₄ that $T_c \approx T_K$, we estimate $\Gamma = -(B/T_c)\partial T_c/\partial P \approx 56$ where we have used $\partial T_c/\partial P = -2 \text{ K kbar}^{-1}$ [14] and $B = 1120 \text{ kbar}$ [15]. Hence, while it is reasonable to speak of the YbInCu₄ valence transition as a “Kondo Collapse”, it is not a “Volume Collapse” driven by a large change in cell volume as for Ce.

In addition to the issue of the relation between the phase transitions in Ce and YbInCu₄, a further question is why the valence transition is unique to YbInCu₄ in the larger set of YbXCu₄ compounds ($X = \text{Ag, Au, Pd etc.}$ [16]) that grow in the same C15b crystal structure. A clue to the origin of the transition comes from the observation that the compounds RInCu₄, where R is a heavy rare earth, are semimetals with low carrier density and large Hall coefficients [17]. In a recent study [4] of YbIn_{1-x}Ag_xCu₄ alloys, we have shown that the Hall coefficients R_H in LuAgCu₄, YbAgCu₄ and in the low temperature state of YbInCu₄ have values ($\sim 10^{-10} \text{ m}^3/\text{C}$) typical of ordinary metals, but R_H is anomalously large ($-[4-6] \times 10^{-9} \text{ m}^3/\text{C}$) in LuInCu₄ and in the high temperature state of YbInCu₄ ($-[4-8] \times 10^{-9} \text{ m}^3/\text{C}$). Hence the carrier density changes at the phase transition; this changes the density of states at the Fermi level $N(\epsilon_F)$ and consequently changes the Kondo temperature $T_K \sim \exp[-|E_f - \epsilon_F|/(2J + 1)\Delta]$ which depends sensitively on $N(\epsilon_F)$ through the $4f$ -conduction hybridization strength $\Delta = V_{fk}^2 N(\epsilon_F)$ as well as on $\Delta\epsilon = (E_f - \epsilon_F)$, the distance from the Yb $4f$ level to the Fermi level and the degeneracy ($2J + 1 = 8$ for Yb). Our hypothesis is that specific features of the RInCu₄ band structure allow for two nearly degenerate states: a metallic state with strong hybridization and a semimetallic state with weak hybridization.

In this paper we report measurements of the Hall coefficient R_H for a set of C15b YbXCu₄ and LuXCu₄ compounds ($X = \text{Au}$ [16], Zn , Cd [18], Tl [18], Mg). The

results show that the Hall coefficients have small values characteristic of normal metals in every case. This means that low carrier density is unique to RInCu₄. This observation allows us to hypothesize that the valence transition (which is also unique to YbInCu₄) is connected with the existence of a quasigap, which is a common feature in the band structure [19, 20] of C15b RInCu₄ compounds.

2. EXPERIMENTAL DETAILS

Polycrystalline samples of RXCu₄ ($R = \text{Yb, Lu}$ and $X = \text{Au, Zn, Tl, Mg}$) were prepared by sealing the starting materials in evacuated tantalum tubes which were then sealed in evacuated quartz tubes and heated to 1150°C for 12 h, cooled to 800°C and held at that temperature for 7 days. Single crystal samples of RCdCu₄ ($R = \text{Yb, Lu}$) and of YbXCu₄ ($X = \text{Zn, Tl}$ and Mg) were also grown in fluxes by the method outlined in [3]. Using conventional X-ray diffraction we established that all these samples crystallize in the C15b structure. The Hall coefficients were measured using a He-flow cryostat for temperatures in the range 15–325 K. The samples were shaped into thin plates of typical dimension $0.5 \times 2 \times 3 \text{ mm}$. The Hall voltage was measured in fields of $\pm 1T$ at various fixed temperatures using an LR400 resistance bridge and an operating frequency of 16 Hz. Small misalignment voltages were compensated electronically and the magnetoresistance was cancelled by reversing the polarity of the field. The Hall voltage was linear in applied field for $H \leq 1T$.

3. RESULTS AND ANALYSIS

The Hall coefficients R_H of YbXCu₄ and LuXCu₄ compounds are shown in Fig. 1. The Hall coefficients of LuXCu₄ for $X = \text{Au, Zn, Cd, Mg}$ are weakly temperature dependent, small ($-[0.3-1.7] \times 10^{-10} \text{ m}^3/\text{C}$) and negative. (For LuTiCu₄, R_H is even smaller in magnitude, but positive below 25 K; the latter may be extrinsic behavior.) For RXCu₄ there are four formula units in a cell of side $7.1 \text{ \AA}$, so that in sample one-band model a Hall coefficient of $-1 \times 10^{-10} \text{ m}^3/\text{C}$ corresponds to 5.6 electrons per formula unit. This suggests that these LuXCu₄ compounds are good metals. The Hall coefficients of the YbXCu₄ compounds are also relatively small, being in the range $-[1-10] \times 10^{-10} \text{ m}^3/\text{C}$ (with the exception of YbZnCu₄ where R_H reaches the value $-20 \times 10^{-10} \text{ m}^3/\text{C}$ at the lowest temperatures). As for other Yb compounds [21], the temperature dependence of R_H observed in YbXCu₄ is not due to changes in the carrier density, but is associated with skew scattering [22] from the Yb $4f$ electrons which give a temperature dependence of the form $R_H(T) = R_0(T) + \beta\chi(T)\rho(T)$

Fig. 1. Hall Coefficient R_H vs temperature for YbXCu_4 and LuXCu_4 ($X = \text{Au, Zn, Cd, Mg, Tl}$).

where χ is the susceptibility, ρ is the resistivity and β is a constant. While we defer such an analysis to a later publication [23], here we note that for $X = \text{Au}$ [16], Zn [23] and Cd [18] the susceptibility increases with decreasing temperature, so that the results shown in Fig. 1 imply that β is negative, as is often found [21] in Yb compounds. YbMgCu_4 [23] and YbTlCu_4 [18] show broad susceptibility maxima, characteristic of mixed valent compounds; Fig. 1 then implies that β is negative for YbMgCu_4 but positive for YbTlCu_4 . The background (non-4f) contributions $R_0(X)$ can be estimated from the high temperature asymptotic values (where χ is small); these lie close to the values for the corresponding LuXCu_4 compounds. Our basic result is, then, that the RXCu_4 compounds for $R = \text{Yb, Lu}$ and $X = \text{Au, Zn, Cd, Mg}$ and Tl have Hall coefficients that are more than an order of magnitude smaller than the values seen in

semimetallic LuInCu_4 and the high temperature state of YbInCu_4 , which suggests that the RXCu_4 compounds are all good metals.

4. DISCUSSION

We now consider whether the bandstructure of RXCu_4 supports our hypothesis that the phase transition in YbInCu_4 is connected intimately with the high temperature semimetallic behavior and in addition which features of the bandstructure yield our basic result that semimetallic behavior appears to be unique to RInCu_4 in the class of RXCu_4 compounds in the $C15b$ structure. Bandstructures have been reported for RInCu_4 ($R = \text{Yb, Lu}$) [19] and for RAgCu_4 ($R = \text{Yb, Lu}$) YbAuCu_4 and YbPdCu_4 [20]. A sketch of the non-4f density of states common to all cases studied is given in Fig. 2. A large peak due to Cu-d and X-d states resides 2–6 eV below the Fermi level ϵ_F . For most cases the Fermi level lies in a smaller double-peak due to Cu-p , d and X-p , d states, which is of maximum magnitude $\sim 1\text{--}3$ states/eV-atom and of width ~ 1.5 eV. This is separated by a quasigap (of very low density of states) of width 0.5–1 eV from a peak of width 3 eV and magnitude ~ 5 states/eV-atom due primarily to R-5d states and secondarily to Cu-s , p states. For the Yb compounds, the calculations [19, 20] treat the Yb 4f electrons as band states (as opposed to frozen core states) which forces a partial occupancy (of

Fig. 2. Schematic non-4f density of states for RXCu_4 ($R = \text{Lu, Yb}$) compounds in the $C15b$ structure [19, 20] together with the portion of the Periodic Table governing the relevant X . The Fermi level moves from the low energy side to the high energy side of the double-peak p , d structure as the X atom moves to the right in the Periodic Table. For X atoms in columns to the left of In the resulting behavior is metallic. For LuInCu_4 and the high temperature state of YbInCu_4 , the Fermi level lies in the low density of states (quasigap) region and the behavior is semimetallic.

order 13.6) for the $4f$ state; the Fermi level lies near the top of this $4f$ band. The Fermi level moves progressively from the bottom (low energy side) of the double-peak p , d structure for YbPdCu₄, to the middle for YbAgCu₄, LuAgCu₄ and YbAuCu₄ and then to the top (high energy side) for YbInCu₄. Given the similarity of the density of states in all cases and given this trend in the position of the Fermi level it is clear that rigid band concepts apply at least qualitatively. The Fermi level pushes up through the p , d double-peak as the X atom moves to the right in the Periodic Table.

The Fermi level for LuInCu₄ lies in the quasigap [19], which can also be understood as a consequence of rigid band motion: in the calculation for YbInCu₄ the Yb atoms are formally in the $4f^{14-n}(5d, 6s)^{2+n}$ configuration with $n \sim 0.4$ and contribute 13.6 $4f$ electrons and therefore 2.4 $5d$ and $6s$ electrons to the valence band, whereas for LuInCu₄ the Lu atoms are in the $4f^{14}(5d, 6s)^3$ configuration and hence contribute 0.6 more ($5d$, $6s$) electrons to the valence band, pushing the Fermi level up into the quasigap. Closer examination [19] shows the LuInCu₄ is a semimetal, with a closed hole sheet around the W point and a closed electron sheet around the X point, with the number of electrons equal to the number of holes (0.04 per formula unit). We note that the Hall coefficient of LuInCu₄ (which is $-60 \times 10^{-10} \text{ m}^3/\text{C}$ at low temperature [4]) suggests in a one band model that there are 0.09 electrons per formula unit.

There is an important difference between the expected $4f$ states of YbInCu₄ and those calculated in the band structure: the strong intraatomic correlations cause the $4f$ states to be highly localized and description of them as a simple band at the Fermi level is inappropriate. Nevertheless, the difference between the high temperature and low temperature electronic configurations of YbInCu₄ is similar to the difference between the electron configurations of LuInCu₄ and YbInCu₄ in the band calculations in the following respect: the Yb changes from a mixed valent $4f^{13.2}(5d, 6s)^{2.8}$ configuration at low temperature to a trivalent $4f^{13}(5d, 6s)^3$ configuration at high temperature. The observed change in the carrier density at the phase transition suggests that the extra electrons contributed to the valence band at high temperatures push the Fermi level up into the quasigap, just as occurs for LuInCu₄. This provides justification for our hypothesis that by a small increase in electron count (~ 0.1 – 0.2) the system can move the Fermi energy in such a manner as to decrease significantly the density of states $N(\epsilon_F)$ and hence decrease the $4f$ -conduction hybridization strength $\Delta = V_{fk}^2 N(\epsilon_F)$ in such a manner as to cause a large decrease in the Kondo temperature $T_K \sim \exp[-|E_f - \epsilon_F|/(2J + 1)\Delta]$. It is this feature of the

bandstructure which allows for the phase transition in YbInCu₄, as opposed to the sensitivity of the Kondo temperature to changes in cell volume as in Ce.

For X atoms which are in columns of the Periodic Table to the left of In, the Fermi level of YbXCu₄ and LuXCu₄ should be located in the p , d double-peak with a healthy density of states and concomitant metallic behavior. As reported here for $X = \text{Au, Cd, Zn and Mg}$ and as reported elsewhere [16] for $X = \text{Pd and Ag}$ the YbXCu₄ and LuXCu₄ compounds for these X appear to be good metals. The small Hall coefficients seen in LuTiCu₄ and YbTiCu₄ suggest that these are also good metals. This means that position of the Fermi level can't be determined simplistically from the column of the X element in the Periodic Table. The positive value of the skew scattering coefficient in YbInCu₄ may, however, be an indication of significant differences between RTiCu₄ and the other RXCu₄.

Our hypothesis, which in a straightforward way links the experimental behavior to features of the bandstructure, is compelling and general. We are currently measuring the resistivity, susceptibility, specific heat and L_3 X-ray absorption spectra of the YbXCu₄ compounds [23]. This should allow us to determine whether the Kondo temperature and valence can be related to the position of the Fermi level relative the quasigap as required by our hypothesis. More detailed tests of the hypothesis will require such measurements as photoemission, de Haas van Alphen (dHvA) and optical absorption to establish the background band structures and the position of the renormalized f bands.

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REFERENCES

1. Felner, I., Nowik, I., Vaknin, D., Potzel, U., Moser, J., Kalvius, G.M., Wortmann, G., Schmeister, G., Hilscher, G., Gratz, E., Schmitzer, C., Pillmayr, N., Prasad, K.G., de Waard, H. and Pinto, H., *Phys. Rev.*, **B35**, 1987, 6956.
2. Kojima, K., Hayashi, H., Minami, A., Kasamatsu, Y. and Hihara, T., *J. Mag. Mag. Mat.*, **81**, 1989, 267.
3. Sarrao, J.L., Immer, C.D., Benton, C.L., Fisk, Z., Lawrence, J.M., Mandrus, D. and Thompson, J.D., *Phys. Rev.*, **B54**, 1996, 12207.
4. 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., *Phys. Rev.*, **B56**, 1997, 7993.
5. Lawrence, J.M., Shapiro, S.M., Sarrao, J.L. and Fisk, Z., *Phys. Rev.*, **B55**, 1997, 14467.
6. Severing, A., Gratz, E., Rainford, B.D. and Yoshimura, K., *Physica*, **B163**, 1990, 409.
7. Lawrence, J.M., Kwei, G.H., Sarrao, J.L., Fisk, Z., Mandrus, D. and Thompson, J.D., *Phys. Rev.*, **B54**, 1996, 6011.
8. Kojima, K., Nakai, Y., Suzuki, T., Asano, H., Izumi, F., Fujita, T. and Hihara, T., *J. Phys. Soc. Japan*, **59**, 1990, 792.
9. Koskenmaki, D.C. and Gschneidner, K.A. Jr., *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 1 (Edited by K.A. Gschneidner, Jr. and L. Eyring) 337. North Holland, Amsterdam, 1978.
10. Allen, J.W. and Liu, L.Z., *Phys. Rev.*, **B46**, 1992, 5047.
11. Thompson, J.D. and Lawrence, J.M., *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 19 (Edited by K.A. Gschneidner, L. Eyring, G.H. Lander and G.R. Choppin) 383. Elsevier Science B.V., 1994.
12. Naka, T., Matsumoto, T. and Môri, N., *Physica*, **B205**, 1995, 121.
13. Scott, T.E., *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 1 (Edited by K.A. Gschneidner and L. Eyring), 591. North Holland, Amsterdam, 1978.
14. Immer, C.D., Sarrao, J.L., Fisk, Z., Lacerda, A., Mielke, C. and Thompson, J.D., *Phys. Rev.*, **B56**, 1997, 71.
15. Oomi, G., Kagayama, T., Kojima, K. and Hihara, T., *J. Alloys and Compounds*, **207–208**, 1994, 282.
16. Rossel, C., Yang, K.N., Maple, M.B., Fisk, Z., Zirngiebl, E. and Thompson, J.D., *Phys. Rev.*, **B35**, 1987, 1914.
17. Nakamura, H., Ito, K. and Shiga, M., *J. Phys. Condens. Mat.*, **6**, 1994, 6801 and 9201.
18. Hiraoka, K., Kojima, K., Hihara, T. and Shinohara, T., *J. Mag. Mag. Mat.*, **140–144**, 1995, 1243.
19. Takegahara, K. and Kasuya, T., *J. Phys. Soc. Japan*, **59**, 1990, 3299.
20. Monachesi, P. and Continenza, A., *Phys. Rev.*, **B54**, 1996, 13558.
21. Cattaneo, E., *Z. Phys. B – Condens. Mat.*, **64**, 1986, 317.
22. Fert, A. and Levy, P.M., *Phys. Rev.*, **B36**, 1987, 1907.
23. Sarrao, J.L., Fisk, Z., Booth, C.H., Figueroa, E., Lawrence, J.M., Cornelius, A.L., Hundley, M.F., Kwei, G.H., Thompson, J.D. and Bridges, F., unpublished.