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Theory of pressure effects and the correlated-electron behavior of uranium monochalcogenides

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Abstract

Experimentally, hydrostatic pressure experiments provide a very sensitive way to probe the development of magnetic ordering in correlated-electron systems. The recent high pressure experiments of Link *et al.* on UTe provide extremely interesting results. With applied pressure, the Curie temperature T_C for UTe increases from 104 K to a maximum of 181 K at 7.5 GPa and then decreases to 156 K at 17.5 GPa. This experimental behavior is qualitatively what we expect on the basis of our theory of the correlated-electron behavior. Basically, increasing pressure causes increased hybridization which causes an increase in coupling between the moments associated with the relatively localized part of the f spectra density at each lattice site. However, as the pressure increases further, the loss of localized f spectra density caused by the increased merger with the non-f-band density causes a decrease in ordered moment and hence a decrease in T_C. We have performed calculations quantifying the above picture for UTe. First we calculate the pressure dependence of the lattice constant and obtain good agreement with the experiment. Next, at calculated lattice constants we calculated T_C using our correlated-electron theory for magnetic ordering. These results capture the initial increase in T_C resulting from increased hybridization as well as the reversal of this initial increase caused by the loss of localized f density.

In correlated-electron uranium-based materials such as UTe [1, 2] and UPt_3 [3], the change in magnetic ordering in response to hydrostatic pressure has interesting characteristics: the ordering temperature rises with, or at least is insensitive to, pressure initially, while the low temperature ordered moment m_o decreases or indeed plunges dramatically. In the case of the weakly correlated ferromagnet UTe, in the measurements of Link *et al.* [2] T_C increases from 104 K at ambient pressure to a maximum of 181 K at 7.5 GPa and then decreases to 156 K at 17.5 GPa, while the decrease in m_o with the initial pressure in the measurements of Bartholin *et al.* [1], while substantial, is not drastic in comparison with the results of Hayden *et al.* [3] for the heavy-fermion antiferromagnet UPt_3 [3]. For UPt_3 [3], the application of 2.05 kbar pressure causes no observable change in T_N, while m_o is drastically reduced by 50%. If, as in the mean field theory, the ordering temperature, T_{order}, scales with the two-ion coupling J and the low temperature ordered moment m_o, *i.e.* $T_{order} \alpha J m_o(m_o+1)$, then, in both UTe and UPt_3, J increases and m_o decreases with pressure.

In order to understand this behavior, we consider the following effects.

(i) *Localized 5f spectral loss in real space.* When pressure increases, the system responds with the following reactions: the atomic distance decreases, → the volume of the core region reduces, → the core potential becomes less attractive, → the f states diffuse more of their waves outside the core region. Band structure calculations verify this. In such calculations, the core regions are represented by muffin tin spheres. The f waves (partial waves with orbital quantum number $l=3$ within a muffin tin sphere) are singled out and filled up to the fermi level, thus giving the local f electron number n_f. Table 1 shows the results of such calculations for UTe, from which one can see the decrease of n_f with pressure. This decrease in n_f is a result of crystallization: the parts of the f wavefunction at large radial distances (or, outside the muffin tin spheres in band structure calculation) are distorted by the crystal field and lose the f characteristic. A consequence of this real space 5f shell spectral loss is the reduction in the localized f moment.

(ii) *Increase in hybridization.* Hybridization V depends on the integral between the f states $\phi_f(r)$ and extended band states $\psi_{band}(r)$: $V=\langle\psi_{band}(r)|H|\phi_f(r)\rangle$, where $\phi_f(r)$ consists of both $l=3$ orbital wavefunction contained

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TABLE 1. Normalized lattice volume V/V_0 and 5f electron number n_f at different pressures P calculated for UTe from the linearized muffin tin orbital band structure calculation

P (GPa)	Atmospheric	0.98	2.9	5.4	8.3	11.7	15.5	19.7
V/V_0	1.0	0.979	0.952	0.927	0.901	0.877	0.852	0.828
n_f	2.73	2.71	2.69	2.67	2.64	2.62	2.60	2.58

within the muffin tin sphere and crystal-symmetry-dominated wave function diffusing outside the muffin tin sphere. The more $\phi_f(r)$ is diffused in space, the more it overlaps with $\psi_{band}(r)$, and thus the larger the V. As described in (i), pressure causes $\phi_f(r)$ to be more diffused, and thus V grows with pressure. As a consequence, the hybridization-induced two-ion coupling also grows with pressure.

(iii) *Localized 5f spectral loss in energy space.* Without hybridization, the 5f states form a narrow f peak in energy space. When hybridization is turned on, parts of the f waves go to the extended regions in the energy space. This is schematically shown in Fig. 1. The parts of the f waves in the extended regions still keep the f characteristics; however, being extended states, they do not belong to a single atom, but to the whole crystal. To see this in real space, electrons of these parts of the f waves hop around among neighboring atoms, and during their stay on a certain atom they are contained within a muffin tin sphere and are f like in nature. The hopping is via non-f extended bands, a result of hybridization. Thus, the f waves can be viewed as consisting of two parts: the localized f waves in the narrow f peak, and the itinerant f waves in the extended regions. The addition of these two parts of the f waves on a certain atom, after time averaging, gives n_f, the f electron number in the real space. As a consequence, not all of n_f contributes to the stable local f moment; instead, parts of n_f, belonging to the extended states and being itinerant, do not always follow the magnetic polarization of the local moment. Since this

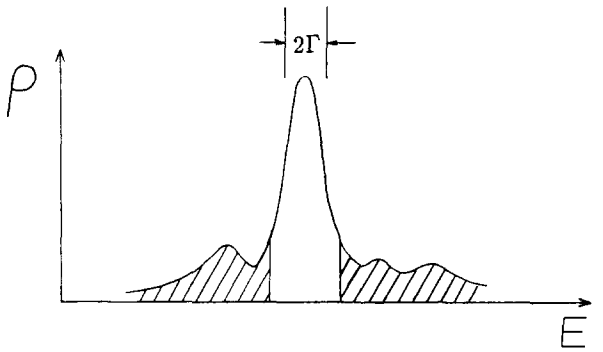

Fig. 1. f spectrum in energy space. The narrow peak, the localized f spectral weight, has a width Γ. The presence of f waves in the extended region is indicated by shading.

effect is hybridization induced, it also grows with the pressure.

We can see from (i)–(iii) that pressure enhances the f spectral loss in real space, which enhances hybridization, which further enhances the f spectral loss in energy space. The f spectral loss in real space reduces the local moment by turning f waves into non-f waves (effects in (i)); the f spectral loss in energy space reduces the local moment by turning localized f waves into itinerant f waves (effects in (iii)). Both effects in (i) and (iii) weaken the magnetic ordering. On the contrary, through increasing the two-ion coupling, hybridization strengthens the magnetic ordering (effects in (ii)), and thus competes with effects in (i) and (iii). The varying magnetic ordering with pressure can be explained by the competition of these effects: the initial increase in T_C is due to the initial winning effect of the mechanism which strengthens magnetic ordering; the ultimate decrease in T_C is due to the eventual changeover of winning and losing effects.

In the following, we quantify this theory using techniques based on the theoretical framework we have developed [4]. As a test case, the calculation is done for UTe. It involves the following procedures.

(1) This part of the calculation is of concern with regard to effects in (i). We perform a sequence of band structure calculations with a series of different lattice constants. We use a full-potential linearized muffin tin orbital (LMTO) band structure (self-consistent relativistic local-density-approximation) calculation. The pressure is calculated by taking the derivative of the total energy with regard to the unit cell volume. The lattice volume change with pressure and the f electron number (in real space) n_f change with pressure are shown in Table 1 and Fig. 2. n_f changes from 2.73 at ambient pressure to 2.58 at 20 GPa, a loss of 0.15 f electrons per atom. Figure 3 shows the density of states (DOS) at three lattice constants (*i.e.* at three pressures). The DOS spectra have two peaks originating from the f states and split by spin–orbit coupling. The peak on the higher energy ($j=\frac{7}{2}$) side is empty. The other ($j=\frac{5}{2}$) peak contains electrons, and the physics of interest occurs there.

(2) This part of the calculation is of concern with regard to effects in (ii). Comparing the three DOS spectra in Fig. 3, one can see that the ($j=\frac{5}{2}$) f peak

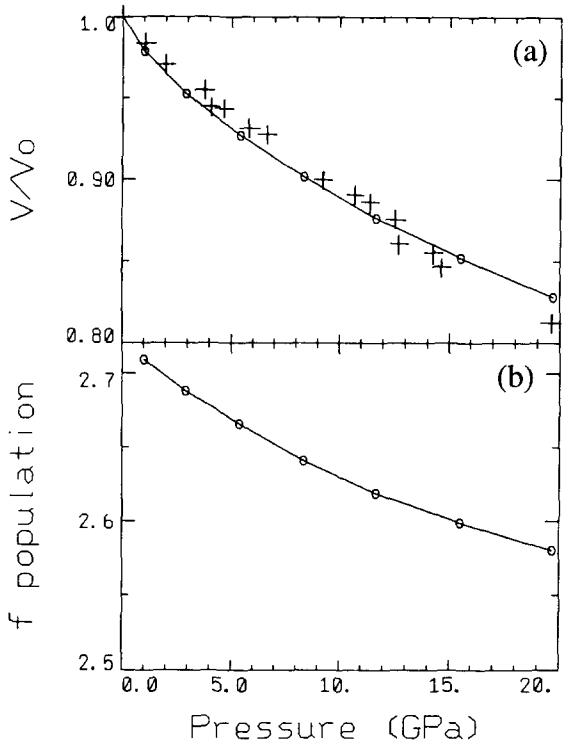

Fig. 2. (a) Normalized lattice volume V/V_0 *vs.* pressure and (b) 5f electron number n_f *vs.* pressure: O, calculated from the LMTO band structure calculation; +, experimental volume data from Gerward *et al.* [5].

becomes wider when the lattice constant is smaller (pressure is greater). We define the width Γ for the f peak:

$$\Gamma = \frac{[\int_{\rho>\rho_{\text{cut-off}}}(E-E_{\max})^2\rho(E)\,dE]^{1/2}}{\int_{\rho>\rho_{\text{cut-off}}}\rho(E)\,dE} \tag{1}$$

where ρ is the DOS and $E_{\max}$ is the energy at the peak $\rho_{\max}$. $\rho_{\text{cut-off}}$ has to be chosen in the calculation, since the division into the localized f waves and itinerant f waves is not clear cut. We choose $\rho_{\text{cut-off}}$ to be 15%, 20%, 25% and 28% of the peak value $\rho_{\max}$; results from different $\rho_{\text{cut-off}}$ will be compared below.

Since a bandwidth can be attributed to the interatomic interaction, Γ serves to specify the coupling of f states localized on neighboring atoms. Suppose such coupling only occurs for the first-nearest neighbor; then Γ can be related to the two-ion coupling J in the following way. Consider the Hubbard model:

$$H_{\text{H}} = \left(-t\sum_{\substack{in\\mm'}} c^{+}_{im}c_{i+n,m'} + \text{h.c.}\right) + U\sum_{i,\,m\neq m'} n_{im}n_{im'} \tag{2}$$

where t is the interatomic interaction, U is the on-site Coulomb repulsion, m the magnetic quantum number, i an atomic site, and $i+n$ labels the first neighbors of site i. A tight binding band results from using H_{H}: $E_k = E_0 - t\Sigma_n \exp(-ikR_n)$. For an f.c.c. lattice, this

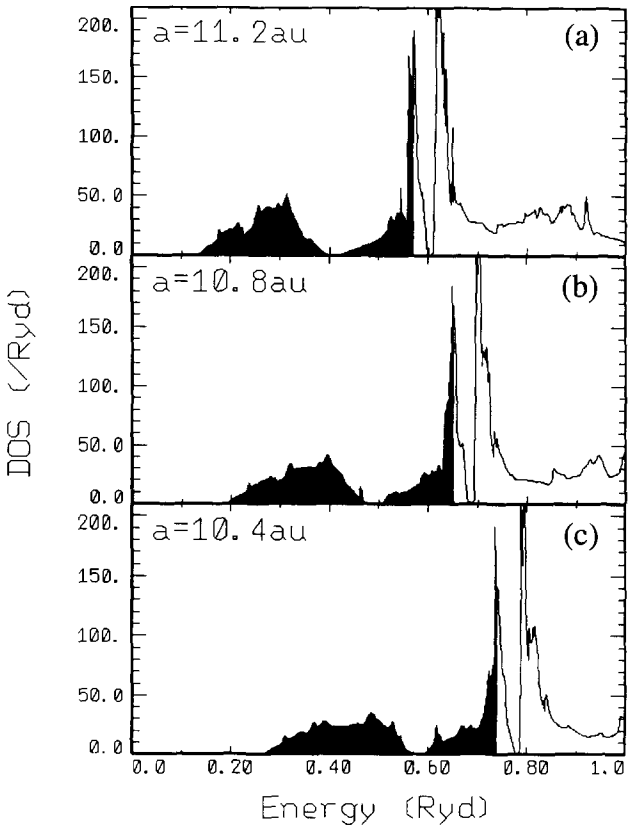

Fig. 3. DOS of UTe, calculated with three lattice constants: (a) $a = 11.2$ au; (b) $a = 10.8$ au; (c) $a = 10.4$ au. The states below the Fermi level are indicated by shading.

band has a width $\Gamma = 1.04t$. This is obtained by projecting E_k onto the energy space using the tetrahedral technique [6]. Thus, calculating Γ from the DOS spectra using eqn. (1) for a real system gives t. Figure 4(b) illustrates the so-calculated t *vs.* pressure. t increases with pressure as expected.

If $U \gg t$, H_{H} can be converted into the following model (see, for instance, ref. 7):

$$H = \left(-t\sum_{\substack{in\\mm'}} c^{+}_{im}c_{i+n,m'} + \text{h.c.}\right) - J\sum_{in} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+n} \tag{3}$$

where $J = t^2/U$. Clearly J is the two-ion coupling. U can be calculated from a supercell scheme [4], which gives $U = 3.4$ eV. With t obtained as above, we can calculate $J = t^2/U$. J *vs.* pressure is illustrated in Fig. 4(c). J also increases with pressure as expected.

(3) This part of the calculation is of concern with regard to effects in (iii). The J interaction is predicated to occur between stable local moments. However, as mentioned above in effect (iii), only the f waves in the narrow f peak in the energy space are localized. The rest of the f waves are itinerant and do not join the local magnetization. We define the localized f spectral weight Z:

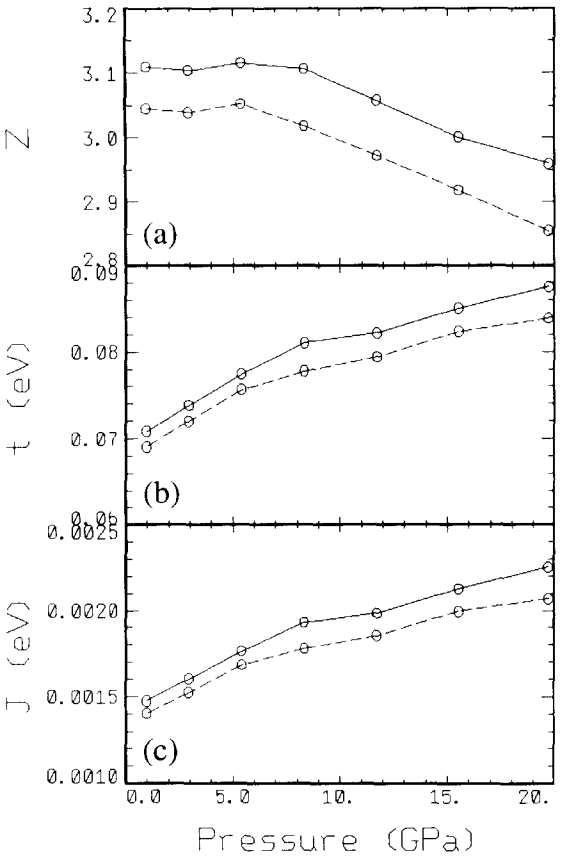

Fig. 4. (a) Localized (corresponding to density of states peak) f spectral weight Z *vs.* pressure, (b) t *vs.* pressure and (c) J *vs.* pressure: —, calculated for $\rho_{\text{cut-off}}=20\%\rho_{\max}$; – – –, calculated for $\rho_{\text{cut-off}}=25\%\rho_{\max}$.

$$Z=\int_{\rho>\rho_{\text{cut-off}}}\rho(E)\,\mathrm{d}E \tag{4}$$

where the choice of $\rho_{\text{cut-off}}$ is taken according to that used in the definition of the width Γ of the f peak. From the DOS spectra, we calculated the Z change using eqn. (4). The results of Z *vs.* pressure are shown in Fig. 4(a).

UTe is close to an f^3 configuration. When an f^3 atom changes to the f^2 configuration, one unit of charge is moved into the extended band states located in a region surrounding this atom, and hence can screen this atom from magnetic interaction with its neighbors. Consequently, an f^2 atom can be approximated as a magnetically "empty" site. We define a baseline Z_0 which corresponds to the situation that the system is in the f^2 configuration. Then $Z-Z_0$ gives the fraction of atoms which are in the f^3 configuration. Since our purpose is to see the change with pressure, we arbitrarily suppose that UTe is completely in the f^3 configuration at ambient pressure, *i.e.* $Z-Z_0=1$. With this setting of Z_0, the fraction of magnetically "empty" sites changes from 0 at ambient pressure to 0.15–0.2 at 20 GPa, depending on the choice of $\rho_{\text{cut-off}}$.

The influence of localized f spectral loss on magnetic ordering can be simulated by an Ising model with holes. We use an Ising model in order to capture the very anisotropic nature of the two-ion hybridization-mediated interaction [4] in a simple way; in future work we plan to treat this anisotropy more realistically as has already been done at ambient pressure [4]. In this model, each lattice site fluctuates between being occupied by a moment or empty; the ratio of the average number of empty sites (holes) to the number of total sites is the fraction of magnetically "empty" sites in UTe; all the occupied sites are coupled to their nearest neighbors by an Ising interaction J, provided that the neighbor is also occupied, while the holes do not couple to any sites.

Computer simulation calculates the curve of free energy *vs.* total moment m of the Ising lattice at different temperatures. When the temperature is below T_C, the curves have double minima where $m\neq 0$; above T_C, the curves have a single minimum at $m=0$ (Fig. 5). This provides the method of calculating T_C. By putting different numbers of holes in the Ising lattice, one can calculate the dependence of T_C on the hole fraction. The results of simulation show that T_C decreases linearly with the hole fraction $1-(Z-Z_0)$.

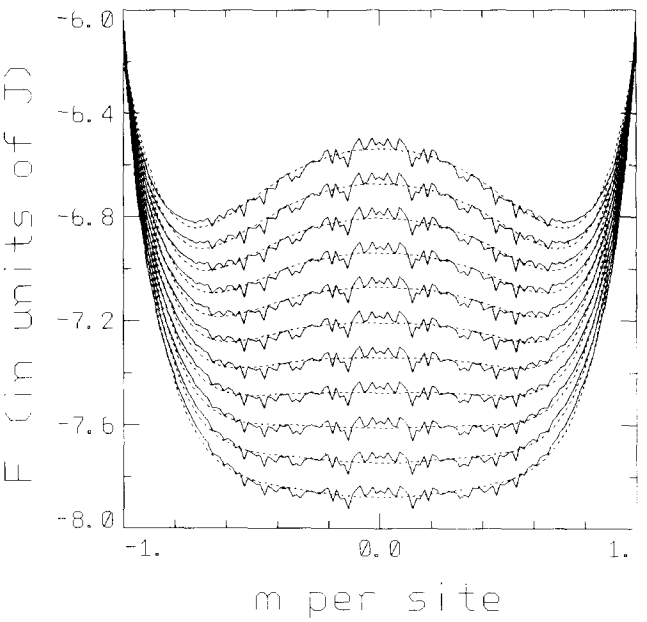

Fig. 5. Free energy F *vs.* magnetization m at temperatures below and above T_C calculated from a computer simulation with an $8\times8\times8$ f.c.c. Ising lattice. The free energy (per site) is in units of coupling J. —, raw data from simulation; – – –, results of the least-squares fitting to smooth out the noise. The curve on the top is for $T=9.0\,J$, and each of the curves below is for a temperature increment of $0.2J$ from the temperature corresponding to the curve above it. With increasing temperature, the double minimum disappears and m becomes zero at $T_C=10.5J$. (This is for the case of no holes.)

With the two-ion coupling J, the localized f spectral weight Z, and their relation to the ordering temperature T_C so obtained in parts (1)–(3), we calculate T_C *vs.* pressure. The results are shown in Fig. 6. Comparing with experiment, the initial increase in T_C is well predicted. Above 7.5 GPa, the calculated curves flatten and do not go down as drastically as in the experiment. These results reflect parts of the competing effects as described at the beginning of this paper.

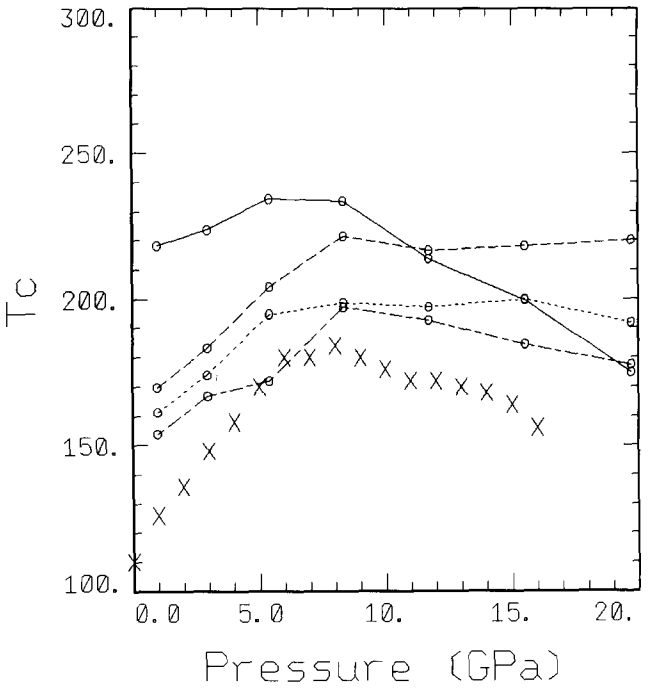

Fig. 6. T_C *vs.* pressure: ——, calculated for $\rho_{cut\text{-}off} = 15\%\rho_{max}$; — — —, calculated for $\rho_{cut\text{-}off} = 20\%\rho_{max}$; – – – – –, calculated for $\rho_{cut\text{-}off} = 25\%\rho_{max}$; — — —, calculated for $\rho_{cut\text{-}off} = 28\%\rho_{max}$; ×, experimental data from Link *et al.* [2].

In conclusion, our calculation for UTe captures the pressure-probed effects, namely the f spectral loss in real space and energy space and their interplay with hybridization, and their influence on the change in magnetic ordering. Further investigation is needed to explain the abruptness of the transition from increasing T_C to decreasing T_C.

Acknowledgments

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