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PANEL I

Aspects of the 5f (de) localization

Discussion leader: A. J. Freeman

Introduction. — The panel was charged by the discussion leader to address themselves to three main areas: (i) theoretical and experimental evidence for/against localization or delocalization of 5f electrons in the actinides; (ii) relevant (physical and chemical) concepts; (iii) applicability of the H. Hill diagram for understanding phenomena in different systems. They were also asked to consider open questions from the floor.

We present here a summary of the extensive discussion organized according to the outline given above rather than in a chronological order.

1. Theoretical and experimental evidence for/against localization. — 1.1 THEORETICAL. — In principle, the theoretical approach implies the inclusion of the proper combination of itinerancy and correlation (Cooper), as e.g., in the extended Hubbard model (Ionova).

The band structure (or itinerant) approach gets in trouble if, upon change of configuration, the eigenvalue changes more than W the effective bandwidth (Koelling).

Spatial 5f distributions which show evidence for the change from delocalization to localization in the actinide metals was presented (Freeman) (Fig. 1).

Since no unique model can account for both static and dynamic phenomena, the question of localization/delocalization cannot be answered simply by a yes or no (Lindgård).

1.2 EXPERIMENTAL. — There was fairly large degree of agreement on the fact that evidence can only come from a combination of experimental techniques (Dunlap, Lander), each one sampling a different region (e.g. neutron/hf measurements).

Arguments were presented on localization/delocalization from inspection of atomic volumes (Coqblin, Fig. 2).

Some controversy arose as regards the utility of optical experiments in the present context; e.g. doubt on the possibility of measuring dispersion of the 5f state through photoemission (Cooper). Conversely, optical measurements ask good questions (see § 4, Erbudak).

During the cerium debate (see also § 2), a question as how to measure the number of f electrons across the α-γ transition was raised (Sinha). One possibility is the lattice parameter measurement (Coqblin); it is difficult to distinguish between itinerancy and valency fluctuation experimentally (Johansson), though ESCA could work (Bertaut).

![Fig. 1. — Radial charge density for the lowest f-state (Γ') in γ-U, δ-Pu, β-Am, and β-Bk.](image1)

![Fig. 2. — Variation of the atomic volume along the actinide, lanthanide and transition metal series.](image2)
Correlation between isomer shifts (I.S) and s-f hybridization should be possible (Gal).

2. Relevant concepts. — 2.1 PHYSICAL. — High density \( n(E_f) \) is irrelevant (Cooper) (e.g. photoemission peak at \( E_f \)). For some, spatial distribution is relevant since it is a popular concept (Dunlap).

However, the main emphasize was on the concept of (de) localization in energy:

The rate of change of eigenvalue as a function of occupation number (relative to the dispersion of the state) is a general criterium useful for all types of calculations (atomic, molecular clusters in solids, band structure) (Keller).

In other words, the same concept of the relative magnitude of the one-site Coulomb repulsion \( U \) and the bandwidth \( W \) was stressed (Freeman, Brandow); when \( U < W \) the band model is a valid description whereas when \( U > W \) the band picture is not (Freeman). Also, the distinction localization/delocalization is dependent on the nature of low lying excitations (Brandom).

In general, the distinction between mixed valence and itinerant systems is not clearcut (Sinha); mixed valence concept applies when restricted to cases where only 2 configurations are present in the ground state. This can have dramatic effects on the statistics such electrons would obey and hence on e.g., the \( T \)-dependence of the magnetic susceptibility or the specific heat (Sinha).

Pertinent to this section is the controversy about the \( \alpha - \gamma \) transition in cerium metal. Two points of view emerged: In one (Coqblin), a model for \( \gamma - d - \alpha' \) cerium is based on variation of the 4f electron occupation number (change with pressure). Arguments relying on lattice parameter changes and considerations of the ratio \( U/W \) (4f bandwidth) are used to argue against a Mott transition description (presented by Johansson). In this latter view, the important physics is a Mott type transition with lattice parameter involving not an occupation number change but rather a change in the spatial character of the 4f electron wave function.

Comparisons are then made with the situation in the actinides (large, \( \sim 20\% \) volume change in going from Pu to Am).

For others, lattice parameter change at Mott transition has no implication on 4f occupations; the band calculations by D. Glötzl support the second point of view (Brandom).

Also, complete opposition between superconductivity and magnetism is not necessarily true. For example the superconductivity of Am has no implication on 5f localization (Smith); superconductivity seems to benefit from the existence of f character above \( E_f \) as in La (vs. Sc and Y) and Cs and Ba (vs. Rb).

A criterium which would be useful for experimentalists is: does delocalization (by 5f → 6d promotion or hybridization) conserve or destroy the magnetic moment? (Bertaut).

2.2 CHEMICAL (F. L. Carter). — The valence band model is used by chemists when forming hybrid bands between an actinide and its neighbour, their radial part is extended whereas the remaining orbitals are contracted; the f orbitals are thus seen at the same time to be both localized and delocalized.

The Mott transition can be viewed in terms of bond hybrids and bond order.

3. Applicability of Hill diagram. — There was little discussion of this question, it having been agreed that this topic would be covered more in Panel III.

— For the \( U_x X_2 \) type compounds at least the Hill diagram tends to be valid (Troc).

— The respective lattice parameters for NpSn, and NpPd, are 4.9 and 4.0 \( \text{Å} \); however Mössbauer effect supports the view that NpSn, is itinerant and NpPd, localized (Gal).

4. Open questions. — There were a considerable number of questions raised from the floor; what follows is intended to give the flavor of the questions raised.

In view of emphasizing the possible pertinence of optical experiments, it was recalled that photoelectron spin polarization measurements shed light on 3d electrons, and several questions arose (Erbudak):

— A high negative spin polarization found in UTe and USE is interpreted in terms of 6d electron magnetic moments being antiparallel to the 5f's? Is this superexchange interaction to be interpreted as itinerant 5f's?

— The 6d band occupation does not change much from USb to UTe; this can be understood in terms of 5f electrons in USb participating in bonding. Will this fact give a clue on the nature of f electrons?

Concerning the approaches to enhanced Pauli paramagnets, and more precisely the neutron results on UAl, (border line in Hill diagram), several questions were raised (Steglich).

The first set of questions relates to the \( \chi(T) \) behaviour (Fig. 3).

Fig. 3. — Actinide enhanced Pauli paramagnets susceptibility curve.
— Physical origin of $T^*$; role of many-body effects on both sides?
— Does the Curie-Weiss effective moment provide a criterion for (de) localization? (also, the high temperature entropy?).
— If $A_{cr} > T^*$, could crystal field excitations be observed on either side?

The other set of questions relates to figure 1 of [1] dealing with neutron magnetic scattering (Loewenhaupt).

— What can we learn about 5f bandwidths from the width of the quasi-elastic line?
— How can one explain its temperature dependence?

5. Conclusion. — The lively nature of the questions and discussions indicate a very active and evolving view of the nature of (de) localization of 5f electrons. The fact that so many questions were raised without complete answers indicates that the actinides, like the transition metals for which the same questions have been raised for the last 40 years, are complex systems for which much more work remains.

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References