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RELATIVISTIC ELECTRONIC BAND STRUCTURE AND PROPERTIES
OF THE HEAVIER ACTINIDES: A SECOND RARE-EARTH SERIES*

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ABSTRACT

The heavier actinides i.e., Am and beyond, have been studied by means of RAPW calculations and are found to differ dramatically from the lighter metals: the 5f electrons appear to be more localized spatially, overlap only weakly with their 5f neighbors and show band widths which are small relative to the Coulomb correlation energy. Hence, just as in the case of the rare-earth metals, the 5f electrons may not be described by the band model. Instead, a localized description is required in which, as in the rare-earths, Hund's rule intra-atomic exchange coupling produces localized 5f magnetic moments which can be ordered magnetically by indirect exchange interaction.

Until very recently, little was known about the electronic band structure of the actinide metals with which to interpret their magnetic properties. Quite aside from the expected theoretical complications of treating relativistically the complex crystallographic structures formed by these metals, their conduction band structures are expected to be more complicated than that of either the transition metals or the rare-earth metals. Here we report on the fcc phases of these metals. In the lighter actinides, detailed Symmetrized Relativistic APW (SRAPW) studies¹ have shown that the 5f electrons are not well localized (unlike the 4f orbitals in the rare-earth metals) so their itinerant nature makes them hybridize strongly with both the 6d and 7s bands. This strong hybridization of the broad 5f itinerant states with the very broad 6d-7s bands shown in Fig. 1 for fcc plutonium metal results in a band structure which has an overall large effective band width for the (possible) magnetic carriers. (The plane wave state can be seen starting at Γ_6^+ with the parabolic shape. The d states at Γ are the spin-orbit split t_{2g} (Γ_8^+ and Γ_7^+) and the higher e_g (Γ_8^+). All states shown with negative parity at Γ are f-states.) This large f bandwidth makes it energetically too costly to produce any magnetization (flipping of spins); i.e., in the band picture² the kinetic energy penalty of promoting an electron of one spin band into the opposite spin band exceeds the lowering of energy due to exchange interactions (because the effective width is just too great). This same

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qualitative picture appears to hold for all the lighter actinide metals which show no magnetic ordering.

In the lighter actinides, the itinerant or band point of view is applicable because of the large overlap between neighboring 5f electrons resulting in their band widths exceeding the Coulomb correlation energy. By contrast, the 4f electrons in the rare-earths are highly localized, do not overlap neighbors appreciably and form a very narrow energy band in the solid whose effective width is much smaller than the Coulomb correlation energy.³ Thus unlike the case of the 5f electrons in these actinides, the 4f electrons may not be treated as band electrons because of the large errors ($\sim 10-15$ eV) introduced by neglect of the intra-atomic Coulomb correlation terms.

We have investigated the heavier actinide metals Am, Cm and Bk by means of the SRAPW method. The effects of varying α , the parameter multiplying the free electron exchange potential ($\rho^{1/3}$) and atomic starting configurations (relative number of occupied 5f, 6d and 7s electrons) on the resulting band structure was studied--all in the "warped" muffin tin approximation. Since space does not permit a detailed presentation of our results, a summary will be given. Fig. 1 includes the band structure of these heavier metals obtained with $\alpha = 2/3$ (the Kohn-Sham Gaspar exchange approximation). We have found that there is a sharply increased localization of the 5f electrons in these metals with increasing atomic number, i.e., greatly decreased overlap and rapid narrowing of their band widths. (This localization is found to be much greater in the $\alpha = 1$ calculations, which we feel, however, are not as physically meaningful.) These much narrower bands do not hybridize greatly with the 6d and 7s itinerant bands. Further, since the Coulomb correlation is large relative to the effective band width, the itinerant (or band) description is no longer valid. Instead the localized description of the ionic 5f electrons (i.e., large spin-orbit and Hund's rule coupling of L, S and J--all maximized--interacting with their environment through the crystalline electric field and the exchange interactions via the conduction electrons) appears now more appropriate, as in the case of the rare earth metals. Indeed, an apt description of these metals is that they appear to form a second rare-earth series with all that implies. For magnetism we may well expect for the heavier actinide metals the diversity (and complexity) of magnetic ordering phenomena found for the rare-earth metals. It thus appears to be a new fruitful (but difficult) area for magnetic research.

One final remark should be made about the Cm band structure where the f-localization is not nearly as pronounced as for either Am or Bk. This is due to the anomalously small lattice constant reported for Cm. Had we derived an effective lattice constant from the α phase (dhcp) near neighbor distances, the resulting f-band widths would have been as small as for the Am and Bk.

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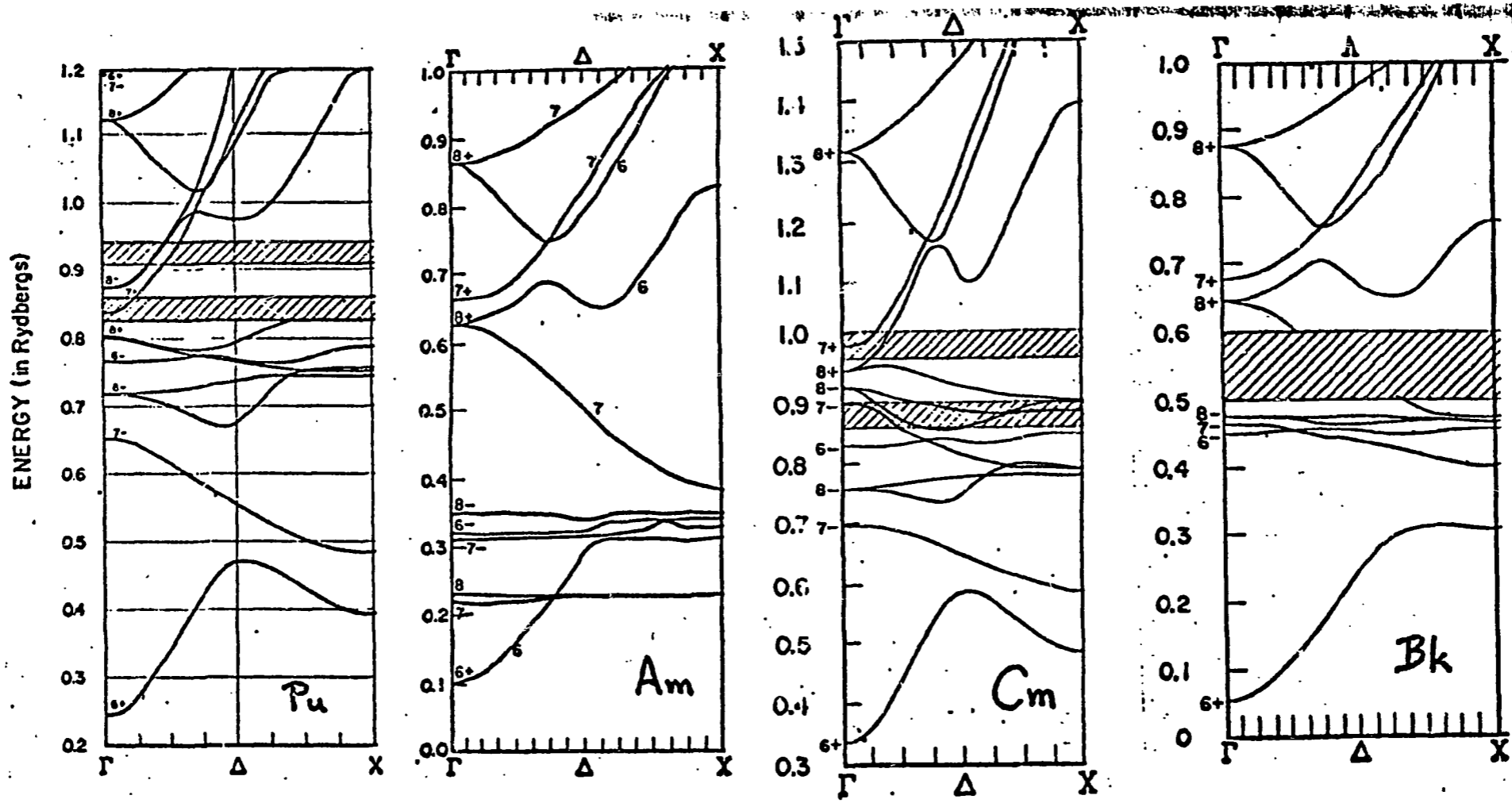


Fig. 1 Energy Bands in (100) direction for fcc Pu, Am, Cm, and Bk