It is convenient to refer to a ferroelectric as being *primitive* or *complex* according to whether the number of equivalent unique ferroelectric directions of its species is 1 or larger. We note as a "theorem" that the paraelectric phase transition of every primitive ferroelectric can be of either first or second order. (We shall in the future discuss the relationship between the concepts of primitiveness and complexity for *ferroelectrics* and those for *ferro-paraelectric phase transitions*.)

A crystal which can become ferroelectric, in the most general case, assumes several different ferroelectric phases in different regions of temperature. It is presumed that in most cases—but not all—the prototypes of such ferroelectric phases are one and the same. (It may also be possible that one crystal has two or more different prototypes in different regions of temperature.) In future when a systematic investigation is made into ferro-ferroelectric phase transitions, the concepts of prototypes and species (and minor species) will play an important role.

Relativistic Energy Bands for Thorium, Actinium, and Lutetium*

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(Received 22 December 1965)

The electronic energy bands have been calculated for Lu, Th, and Ac using the relativistic augmented-plane-wave method. The importance of the relativistic effects in the rare earths is typified by the results for Lu which show that the details of the Fermi surface will be altered considerably by these effects. As indicated by the bands for Th and Ac, the relativistic effects will be even more striking for the actinide series.

WE have calculated the electronic energy bands in Lu, Th, and Ac, with particular reference to relativistic effects. There is currently considerable interest in the electronic structures of both the lanthanides and the actinides, and it is apparent from our results that it is essential to consider such relativistic effects in the interpretation of any experimental results. We have studied Lu because it is the heaviest of the lanthanides and has approximately the same electronic structure as Gd, Tb, Dy, Ho, Er, and Tm. Hence, the discussion for Lu should be applicable to all of the heavier $4f$ rare earths, with the exception of Yb which has a different crystal structure. Th and Ac were studied because they are not complicated by the presence of a slightly filled $5f$ band which would require very careful consideration of the self-consistency of the crystal potential. Thus, attention can be concentrated on the rather striking relativistic effects manifested in these heavy elements.

The energy bands were computed using the relativistic augmented-plane-wave (APW) method[1] which has already been successfully applied to tungsten[2] and lead.[3] The potential was constructed from the relativistic atomic self-consistent-field calculations of Liberman, Waber and Cromer.[4] The importance of treating the atomic calculation relativistically has been discussed

by these authors and by others.[5] Exchange was treated in the Slater $\rho^{1/3}$ approximation,[6] both in the atomic calculations and in the construction of the muffin-tin
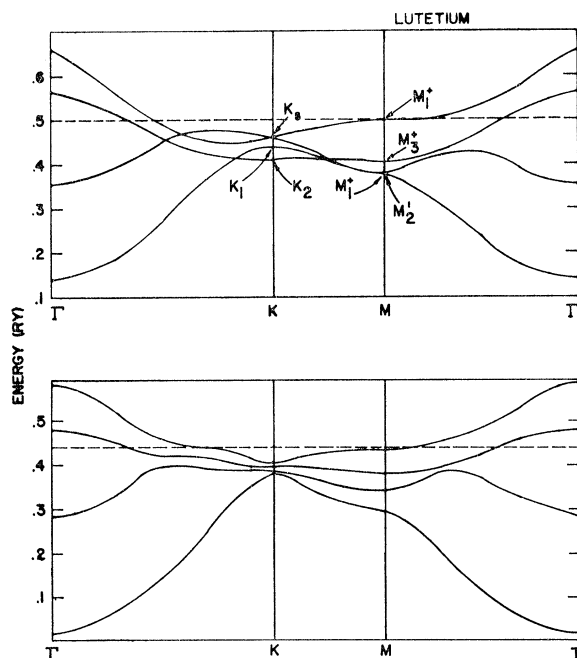

FIG. 1. Nonrelativistic (upper) and relativistic (lower) energy bands for lutetium. The dashed lines give the approximate Fermi energy.

* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1840.

[1] T. L. Loucks, Phys. Rev. **139**, A1333 (1965).

[2] T. L. Loucks, Phys. Rev. Letters **14**, 693 (1965).

[3] T. L. Loucks, Phys. Rev. Letters **14**, 1072 (1965).

[4] D. Liberman, J. T. Waber, and Don T. Cromer, Phys. Rev. **137**, A27 (1965).

[5] R. G. Boyd, A. C. Larson, and J. T. Waber, Phys. Rev. **129**, 1629 (1963).
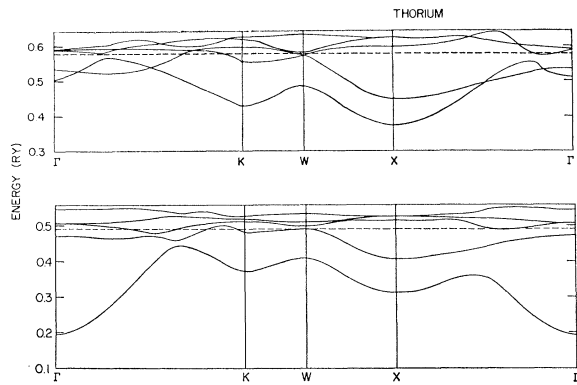
[6] J. C. Slater, Phys. Rev. **81**, 385 (1951).

FIG. 2. Nonrelativistic (upper) and relativistic (lower) energy bands for thorium. The dashed lines give the approximate Fermi energy.

potential for the metals. Our results for the three elements are shown in Figs. 1, 2, and 3. In each of these figures the relativistic energy bands are in the lower half, while the upper half shows the band structure in the nonrelativistic limit.

The nonrelativistic energy bands for Lu in Fig. 1 are very similar (beneath the Fermi energy) to those calculated for Gd by Dimmock and Freeman.[7] Their results are reproduced for comparison in Fig. 4. The primary relativistic effect is simply the lifting of degeneracies by the spin-orbit interaction. We see here a very good example of the dependency of this interaction on the wave vector of the electronic state. At the symmetry point M (in the Brillouin zone for the hcp crystal structure) the splittings are much greater than at K. This can be understood qualitatively from group theoretical considerations. The single group representations of the nonrelativistic levels have been indicated in Fig. 1.[8] The corresponding double-group representa-
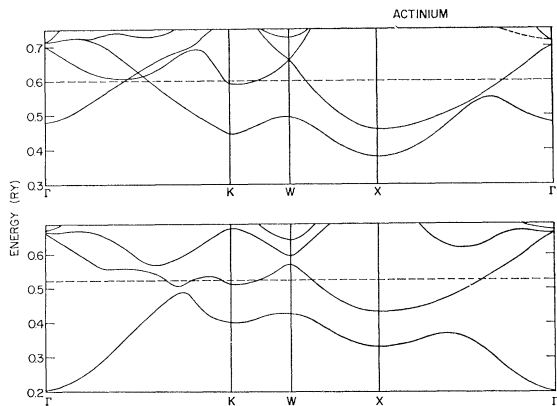

FIG. 3. Nonrelativistic (upper) and relativistic (lower) energy bands for actinium. The dashed lines give the approximate Fermi energy.

[7] J. O. Dimmock and A. J. Freeman, Phys. Rev. Letters 13, 750 (1964).

[8] J. O. Dimmock and A. J. Freeman (private communication).

tions for these levels are given by Elliott.[9] At the point K, for instance, we find $K_1 \to K_7$, $K_2 \to K_8$ and $K_5 \to K_8 + K_9$. The doubly degenerate level is therefore split by the interaction between the two K_8 levels, one from K_2 and one from K_5. The K_7 and K_9 levels, however, do not interact with each other or with the two K_8 levels, so that the net effects at the point K are not large. At the symmetry point M there is a different situation. The group representations are related according int to $M_1^+ \to M_5^+$, $M_2^- \to M_5^-$ and $M_3^+ \to M_5^+$. There are 3 levels with M_5^+ symmetry which interact and the bands are considerably affected. The actual positions of the levels are determined, of course, not by the spin-orbit interaction alone. Other relativistic effects such as the stronger binding of states with low orbital angular momentum also enter our final results since the complete Dirac Hamiltonian has been used.

The features of the Fermi surfaces of the heavier $4f$ rare earths are determined by the third and fourth bands shown in Fig. 1. The relativistic effects on these bands should be strongly reflected in the exact shapes of the Fermi surfaces. The effect that these changes in the energy bands have on the Fermi surfaces is being determined, but these calculations are quite lengthy and will be reported at a later date.

Next let us consider the energy bands for Th and Ac as shown in Figs. 2 and 3. Here the relativistic effects are quite striking. Notice that for both metals the lowest energy state is at the symmetry point X for the nonrelativistic bands. However, in the relativistic calculation there is a tendency for the states of lowest angular momentum to be more tightly bound. Thus at Γ, the point of highest symmetry in the Brillouin zone, an s-like level has been pulled down by at least 0.2 Ry with respect to the other bands. If we use the energy difference between the lowest energy state and the second level at the symmetry point W as a measure of the bandwidth in Th, this quantity is about 0.3 Ry for the relativistic bands compared to 0.2 Ry for the nonrelativistic bands. It should be possible to observe such a large effect experimentally from, for instance, soft x-ray emission spectra. We are not aware of any such data currently available.
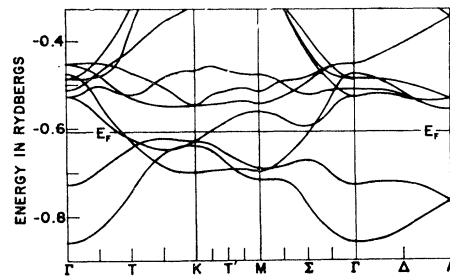

FIG. 4. Nonrelativistic energy bands for gadolinium from Dimmock and Freeman (Ref. 7).
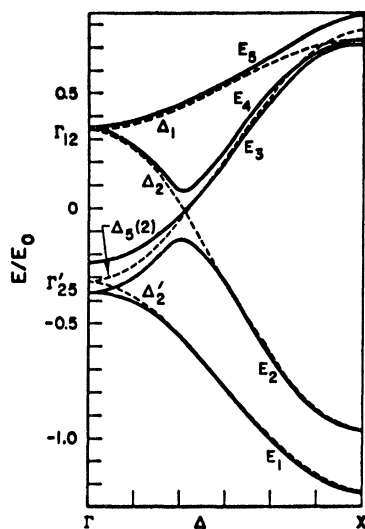
[9] R. J. Elliott, Phys. Rev. 96, 280 (1954).

FIG. 5. Energy bands from Γ to X for thorium from Lehman (Ref. 10). The dashed lines are those with no spin-orbit coupling and the solid lines are those including spin-orbit coupling.

FIG. 6. Energy bands from Γ to K for thorium from Lehman (Ref. 10). The dashed lines are those with no spin-orbit coupling and the solid lines are those including spin-orbit coupling.

Prior to these calculations the most recent theoretical work on Th was reported in 1959 by Lehman.[10] He used a parametrized model which included spin-orbit effects and was based upon Kohn's variational principle.[11] The method was similar in some respects to the Slater-Koster[12] tight-binding interpolation scheme and approximated each plane surface of the unit cell by a spherical cap of equal area. His results, which included only the d bands, are shown in Figs. 5 and 6. We see the triply degenerate Γ_{25}' level and the doubly degenerate Γ_{12} level which are characteristic of d bands at the symmetry point Γ. The spin-orbit interaction splits Γ_{25}' into a single level Γ_7^+ and a doubly degenerate level Γ_8^+. The splitting of the triply degenerate level is also seen in our bands shown in Fig. 2. The important feature of our bands, however, is that these levels are *above* two other valence bands which were not even considered in Lehman's work.

The relative position of our d bands with respect to the lower bands can be understood qualitatively from the results of atomic self-consistent field calculations. For instance, in the Hartree-Fock-Slater atomic calculation of Herman and Skillman[13] the $6d_{3/2}$ level was found to be at -0.6176 Ry and the $7s_{1/2}$ level at

-0.4785 Ry. These calculations were made self-consistent using a nonrelativistic Hamiltonian, and the resulting levels were corrected for relativistic effects by perturbation theory. Thus, they found the $6d_{3/2}$ level to be lower than the $7s_{1/2}$ level. However, Waber et al.[4,14] have performed similar calculations solving the Dirac central-field Hamiltonian self-consistently and have found the $6d_{3/2}$ level at -0.3970 Ry and the $7s_{1/2}$ level at -0.4300 Ry. Hence, the two levels have nearly the same energy, but the $7s_{1/2}$ is lower in the relativistically self-consistent potential. This has been attributed by these authors to an indirect relativistic effect. The states of lower angular momentum are more tightly bound in the Dirac Hamiltonian, and this causes an adjustment in the self-consistent charge density near the origin which results in different screening for the outer states. Because we have constructed the muffin-tin potential for the metal from the relativistic atomic charge densities, it is not surprising that the d bands are not the lowest valence states.

The relative position of the d bands with respect to the Fermi energy in Th is similar to that found by Mattheiss[15] for the vanadium group, most of the d bands lying just above the Fermi energy. Thorium, however, is fcc while the vanadium group have the bcc structure. It might therefore be possible to examine the relative importance of the structure of the d bands and the crystal structure on, for instance, the phonon spectrum by comparing these metals experimentally.

[10] Guy W. Lehman, Phys. Rev. 116, 846 (1959).
[11] W. Kohn, Phys. Rev. 87, 472 (1954).
[12] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
[13] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).
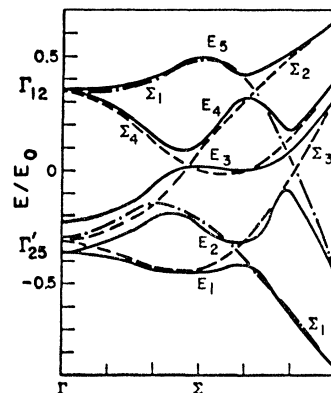
[14] We are very grateful for the cooperation of the group at Los Alamos Scientific Laboratory in making these results available.
[15] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).