INFLUENCE OF SPIN ON ELECTRONIC TRANSFORMATIONS*

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Cerium, the first member of the 4*f* transition elements, undergoes a transformation of its electron configuration at atmospheric pressure and about 120°K, or at room temperature and about 7500 atm. We have now shown that this transition is strongly affected by unpaired spins.

It can be shown from considerations of metallic radii and magnetic properties that this transformation involves the promotion of about 0.5 electron per atom from the 4*f* level to the valence band. The room temperature form of cerium, which we will designate as γ, is face-centered cubic and has a lattice constant of about 5.16 A. γ-Ce at standard pressure and temperature has (0.9 ± 0.1) 4*f* electron, or a valence of 3.1 ± 0.1. The low-temperature (or high-pressure) form, which we will designate as α, is also face-centered cubic but has a lattice constant of about 4.85 A. Similar considerations of magnetic data and metallic radii indicate that α-Ce has 0.4 ± 0.1 4*f* electron, or a valence of 3.6 ± 0.1. β-Ce, which can form only on cooling γ-Ce to about 260°K, is hexagonal with $a = 3.68$ A and $c = 11.92$ A and has approximately the same number of valence and 4*f* electrons as γ-Ce. β-Ce is important in connection with the $\alpha \rightleftarrows \gamma$ transformation because it will form from γ-Ce upon cooling and will not transform to α above 50°K. Thus, the amount of α-Ce present at 50°K will be less, by the amount of β-Ce that is formed, than would normally be expected.

The elements that follow cerium do not appear to undergo a transformation of electron configuration similar to that of cerium, except possibly ytterbium, which may transform at a pressure of about 60 000 atm. Presumably the absence of a $4f \rightleftarrows$ valence band electronic transformation in the elements following cerium is due to a large difference in energy between the 4*f* level and valence band. There are, however, two interesting characteristics of these 4*f* transition elements. (1) They exhibit a small decrease in their metallic radii as the atomic number increases; this is known as the lanthanide contraction. (2) They are either strongly paramagnetic or ferromagnetic and have high magnetic moments, which arise from the number of unpaired 4*f* electrons (except the end number, lutetium, which has fourteen 4*f* electrons, i.e., the 4*f* band is completely filled).

Because the $\gamma \rightleftarrows \alpha$ transformation in cerium is electronic in nature and involves large volume changes (more than 15%), this transformation might be influenced (1) by the magnetic field from a magnetic impurity, or (2) by spin-spin interactions between the 4*f* electron of cerium and the magnetic electrons from a magnetic impurity, or (3) by the size of the impurity atom. A consideration of simple alloying theory indicated that probably all of the rare earth metals, some of the actinide metals, and calcium, indium, magnesium, scandium, and sodium might form extensive solid solution alloys; that is, at least 5 atomic percent of any of these elements would be expected to be soluble in cerium. It would seem, then, that the rare earth metals are ideal solute materials for use in investigating the three points mentioned above.

The $\gamma \rightarrow \alpha$ transformation temperatures of cerium alloys containing 2 at. % of the various rare earth metals are shown in Fig. 1. The transition temperature for our cerium stock is 106 ± 5°K. The data shown in Fig. 1 indicate that a 2 at. % addition of all of the solutes except thulium, ytterbium, and lutetium lower the transition temperature of cerium. In Fig. 2, several possible theoretical curves are shown that may be related to the depression of the $\gamma \rightarrow \alpha$ transformation temperature. A comparison of the curve in Fig. 1 with the curve representing the magnetic moments in Fig. 2 shows that the depression is definitely not related to the dipole moment of the magnetic impurity atom. If it were, we would expect that dysprosium and holmium, instead of gadolinium, would have the greatest effect in depressing the temperature, and that samarium would depress the temperature only a few degrees instead of 17°K. On the other hand, the relationship between the "spin only" curve in Fig. 2 and the experimental data is very good. The metals in the latter half of the series (terbium through lutetium) do not seem to have as great an effect on depressing the transformation temperature as do the metals from the first half of the series (lanthanum through europium), which have the same number of unpaired 4*f* electrons. For example,

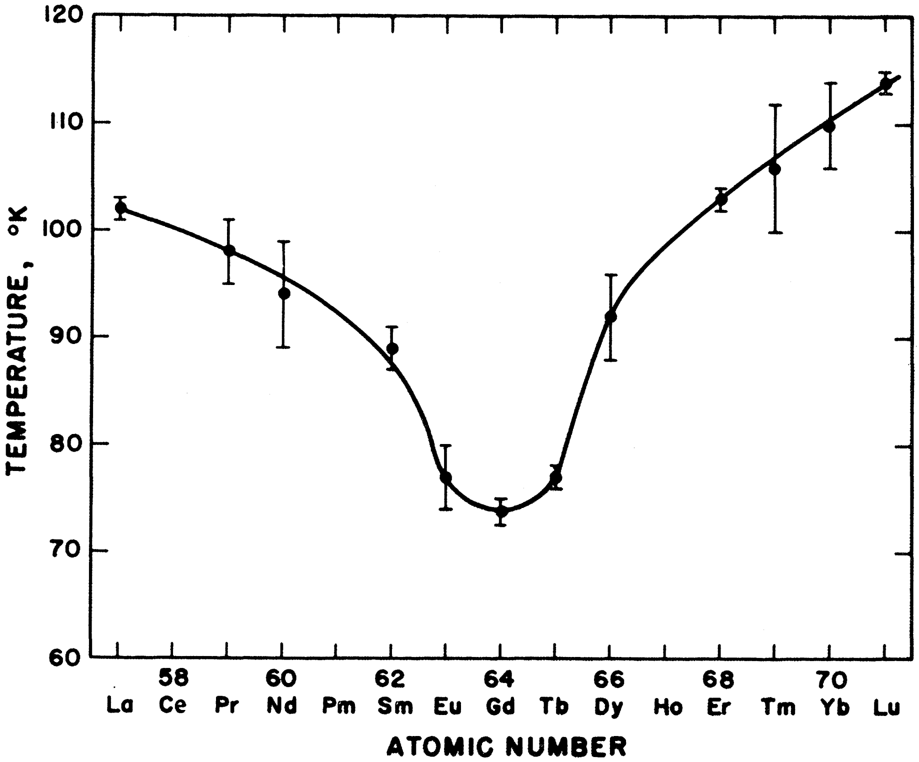

FIG. 1. Influence of 2 at. % rare earth additions on the γ→α cerium transformation temperature.

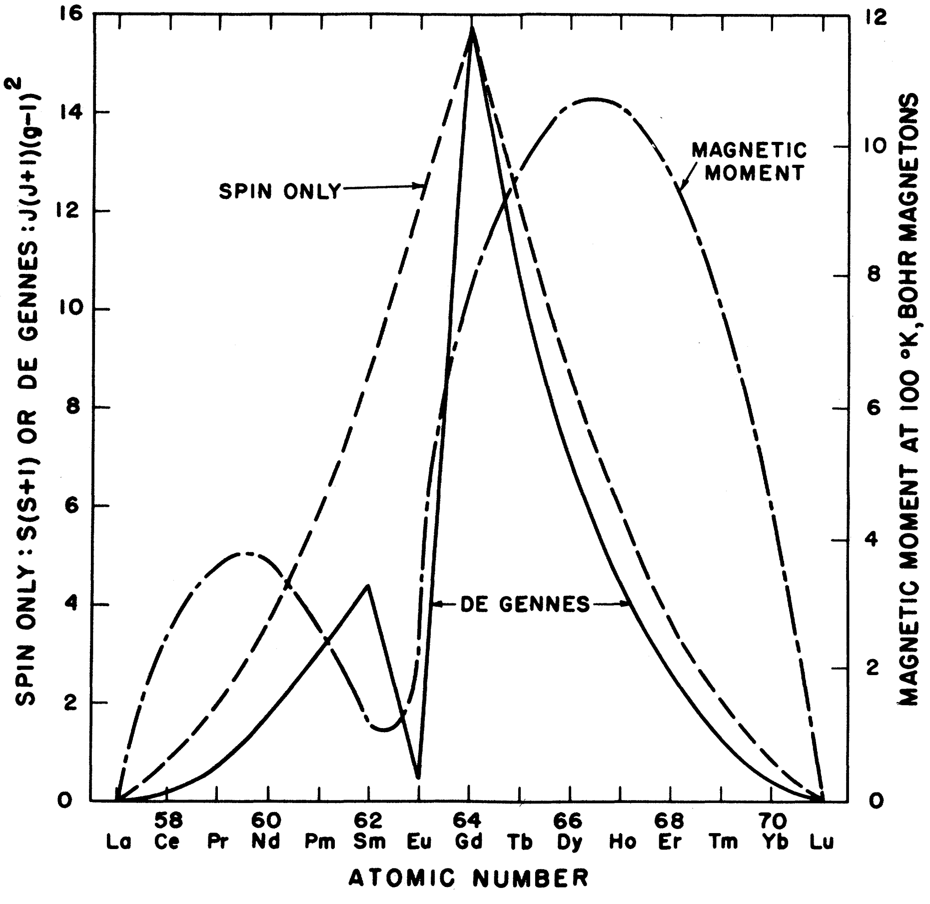

FIG. 2. The magnetic moment, spin only curve, and de Gennes curve, as a function of the atomic number of the rare earth elements.

neodymium with 3 unpaired 4f electrons lowers the transformation temperature 12°K, while erbium, which also has 3 unpaired 4f electrons, lowers the temperature by only 3°K. This unsymmetrical form of the curve shown in Fig. 1 may be due to other factors which simultaneously, along with the spin of the solute atom, influence the transition temperature. These other factors, which play a minor but noticeable role, might be the size and/or the magnetic moment of the solute atom. The third curve, labeled as "de Gennes" in Fig. 2, is a plot of $J(J+1)(g-1)^2$ versus the atomic number. The term $J(J+1)(g-1)^2$ is from a theoretical proposal, made by de Gennes,[1] concerning the proportionality of the Curie points of the heavy rare earth metals (gadolinium through thulium). Suhl and Matthias[2,3] proposed independently that it is also related to the proportionality of the depression of the superconducting transition temperatures of lanthanum alloys containing 1 at. % rare earth additions. It should be noted in Fig. 2 that the de Gennes curve closely follows the "spin only" curve, except for europium, which, in de Gennes' case, should have little or no effect on the transition temperature. Our experimental results, however, indicate that europium fits the "spin only" curve. An objection might be made on the basis that europium behaves as a divalent solute in cerium and, therefore, it might be expected to lower the transition temperature by the same amount as does gadolinium. X-ray analysis of the 2 at. % europium-cerium alloy, however, shows that the lattice constant of the alloy is smaller than that of pure cerium, and indicates that europium is trivalent in this alloy. If europium were divalent, the lattice constant of the alloy would be expected to be larger than that of pure cerium. Similarly, we have found that ytterbium behaves as a trivalent solute in cerium-rich solid solutions.

In cerium alloys containing 2 at. % rare earth metals, the dependence of the $\gamma \rightarrow \alpha$ transformation temperature on the number of unpaired 4f electrons of the rare earth solutes is similar to the dependence of the superconducting transition temperature on the number of unpaired 4f electrons of the solute atoms in lanthanum alloys containing 1 at. % rare earth additions. This suggests that the mechanisms involved in both cases are similar. For the lanthanum alloys, Suhl and Matthias[2,3] have proposed an s-f interaction to explain the observed behavior. We believe that the dominant mechanism in the cerium alloys is an indirect f-f interaction via conduction electrons, and that the larger the 4f contribution from the solute atom (i.e., the greater the number of unpaired 4f electrons) the lower the transition temperature.

We have also examined these same cerium alloys at high pressures and have found that all of the rare earth solutes raise the transformation pressure, but only in proportion to their size. That is, for constant compositions, the larger the size of the solute atom the greater the elevation of the transformation pressure. If the number of unpaired 4f electrons has any effect at room temperature and high pressure, it is so small that we were unable to detect it.

In summary we wish to reiterate that the transformation of electron configuration in cerium-rich alloys at low temperatures is dependent upon the number of unpaired 4f electrons of the solute atom, and that this phenomenon is similar to (1) the depression of the superconducting transition temperature of lanthanum-rich alloys by rare earth solutes,[3,4] (2) the variation in the Curie points of the rare earth AB_2 Laves phase compounds (A = a rare earth and B = ruthenium, osmium, or iridium),[5] and (3) the variation in the Curie points of the heavy rare earth metals.[1]

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[1] P. G. de Gennes, Compt. rend. 247, 1836 (1958).

[2] H. Suhl and B. T. Matthias, Phys. Rev. 114, 977 (1959).

[3] B. T. Matthias, H. Suhl, and E. Corenzwit, J. Phys. Chem. Solids 13, 156 (1960).

[4] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters 1, 92 (1958).

[5] R. M. Bozorth, B. T. Matthias, H. Suhl, E. Corenzwit, and D. D. Davis, Phys. Rev. 115, 1595 (1959).