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Correlation between d-Band Occupancy and Crystal Structure in the Rare Earths

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The rare-earth crystal structure sequence hcp→ Sm-type→ double-hcp→ fcc observed for decreasing atomic number and increasing pressure is quantitatively correlated with the d-band occupancy through the d-band energy contribution to the total energy. Self-consistent calculations show that the number of d electrons is very sensitive to the relative size of the ion core. The theory thus accounts for La's anomalous double-hcp structure and the apparent deviations from the electron-per-atom rules exhibited by certain rare-earth Laves phases.

In a recent paper Johansson and Rosengren[1] found an empirical correlation between the crystal structure of the rare-earth metals and the fraction of the atomic volume occupied by the ion core. In particular, increasing the relative volume of the ion core leads to the crystal-structure sequence hcp→Sm-type→double-hcp→fcc which is observed both for increasing pressure and for decreasing atomic number from right to left across the trivalent rare-earth series.[2-5] However, their attempt to understand this correlation in terms of pseudopotential theory failed. We will show in this Letter that the relative volume of the ion core is in fact a measure of the occupancy of the d band and that it is the d-band contribution to the total energy which drives the lattice through the observed crystal-structure sequence as the number of d electrons changes from about $1\frac{1}{2}$ to $2\frac{1}{2}$. The theory will be shown to account for Lanthanum's anomalous[6] double-hcp (dhcp) structure and for the apparent deviations from the electron-per-atom rules which certain rare-earth Laves phases exhibit.[7,8]

Figure 1 shows the self-consistent energy bands of La in the fcc structure as a function of the atomic volume. They were calculated using Pettifor's[9] development of the atomic sphere approximation[10] in which the main approximation[11] is the neglect of hybridization between the nearly free-electron s band and the tight-binding d band. The

bands display the expected behavior as the atoms are brought together to form the solid. The bottom of the conduction band B_s starts out at very
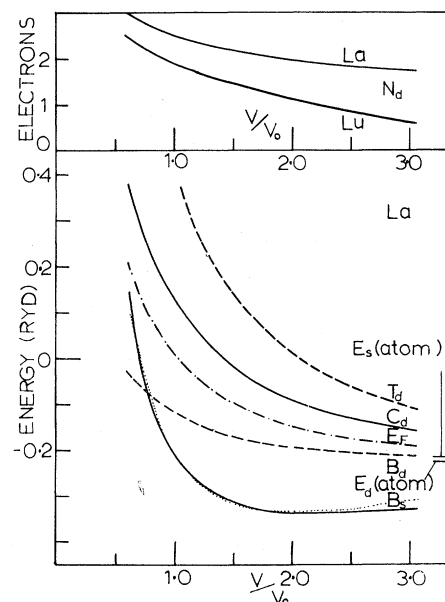

FIG. 1. The energy bands of La about the equilibrium atomic volume V_0 and the corresponding change in the d-band occupancy N_d of La and Lu. T_d, C_d, and B_d are the top, center, and bottom of the d band, respectively, and E_F is the Fermi level. The dotted curve gives the Bardeen-Fröhlich fit [Eq. (1)] to the bottom of the s band B_s.

large volumes by being bonding with respect to the atomic s-level $E_s{}^{\text{atom}}$, but it rises rapidly in energy as the solid is compressed farther about the observed equilibrium atomic volume. In practice, it is accurately fitted (see Fig. 1) by an expression of the Bardeen-Fröhlich[12] form, namely

$$B_s = - (3Z/m_s S)[1 - (r_A/S)^2],\qquad (1)$$

where m_s and S are the effective mass of the s band and the Wigner-Seitz radius, respectively. Z and r_A may be interpreted as the charge and radius of an Ashcroft empty-core pseudopotential,[13] because expression (1) is the potential energy of an electron in the presence of such an effective potential. We find that our self-consistent results for La and Lu are fitted by values of (Z, r_A) given by (0.9, 3.50 a.u.) and (1.01, 2.91 a.u.), respectively, where not unexpectedly[14] the ratio $r_A{}^{\text{La}}{:}r_A{}^{\text{Lu}}$ is the same (within 4%) as that of their observed[15] ionic radii. In order to understand the importance of this ionic contraction across the series on rare-earth properties, we examine briefly the behavior of the tight-binding d band, whose center of gravity C_d and band extremities T_d and B_d are shown in Fig. 1. We see that C_d sweeps up exponentially[16] with respect to the atomic d level as the solid is compressed because of the increase in Coulomb repulsion between the electrons being confined in a smaller region of space. At the same time the d band broadens, an approximate measure of the width being given by the expression[9,10]

$$W_d = 25/(m_d S^2),\qquad (2)$$

where m_d is the d band effective mass. The Fermi energy E_F, obtained by filling the bands with three valence electrons, is shown in Fig. 1 by the chain (dash-dotted) curve. We see that the d-band occupancy is very sensitive to the atomic volome, because in the vicinity of the observed equilibrium atomic volume we are lying in that region of the B_s curve which increases rapidly with compression owing to the large size of the La ion core, so that electrons flow from the nearly free-electron s band to the tight-binding d band. This is clearly illustrated in Fig. 1 by the curves of N_d as a function of volume for both La and Lu. We see that at equilibrium La has approximately 0.6 d electrons more than Lu. We must emphasize that this is the direct result of the differences in the ion-core size between La and Lu and that it is not sensitive to the crystal structure —for example, a self-consistent calculation using the hcp rather than the fcc structure gives a

change in N_d of only 0.007 electrons.

We will now show quantitatively that it is this change in d-band occupancy that drives the lattice through the observed crystal-structure sequence hcp→Sm-type→dhcp→fcc. The difference in total energy U_{tot} between two close-packed structures I and II of equal atomic volume is given to first order[17] in the width of the d band by

$$\Delta U_{\text{tot}}(N_d) = U_{\text{bond}}{}^{\text{I}}(N_d) - U_{\text{bond}}{}^{\text{II}}(N_d),\qquad (3)$$

where

$$U_{\text{bond}}{}^{\text{I,II}}(N_d) = \int^{E_F}(E - C_d)n_d{}^{\text{I,II}}(E)\,dE,\qquad (4)$$

where $n_d{}^{\text{I,II}}(E)$ is the d-band density of states for crystal structure I or II evaluated within the two-center Slater-Koster[18] tight-binding form. N_d is the total number of d electrons. The bonding energy U_{bond} in (4) is the term that Friedel[19] argued was responsible for the parabolic trend in the cohesive energy across the transition-metal series. Andersen[10] has shown that within the atomic sphere approximation the renormalized d-band density of states $W_d n_d(E)$ is canonical in the sense that it depends neither on the lattice constant nor on the d-band energy, but only on the crystal structure. It follows, therefore, that $U_{\text{tot}}(N_d)/W_d$ is also canonical in that it is a function of the filling of the d band only. We have evaluated the densities of states for the four structures fcc, hcp, dhcp, and Sm using the recursion method of Haydock, Heine, and Kelly[20] since this is the most direct way of computing the density of states for the more complex structures. Two-center hopping integrals to nearest neighbors only were included. Figure 2 shows the resulting relative band energies of the hcp, dhcp, and Sm structures with ideal axial ratio with respect to the fcc structure as a function of the d-band occupancy. We see that, as the d band is progressively filled with electrons, we move through the sequence hcp→Sm-type→dhcp→fcc as is experimentally observed. Moreover, this sequence is not sensitive to the choice of axial ratio as is also seen in Fig. 2, where we have given the stability ranges for axial ratios of $c/a = 1.58$, which is typical[1] of the heavier rare-earth metals. The actual energy differences are, of course, very small—being of the order of 1 m Ry/atom (0.3 kcal/mole) for a d-band width of $W_d = 0.5$ Ry.

The so-called anomalous[6] dhcp structure of La is thus seen to be a direct consequence of its having more d electrons than the hcp Lu. In fact, the self-consistent results from our theory (Fig. 1) give $N_d = 2.5$ for La and $N_d = 1.9$ for Lu at their
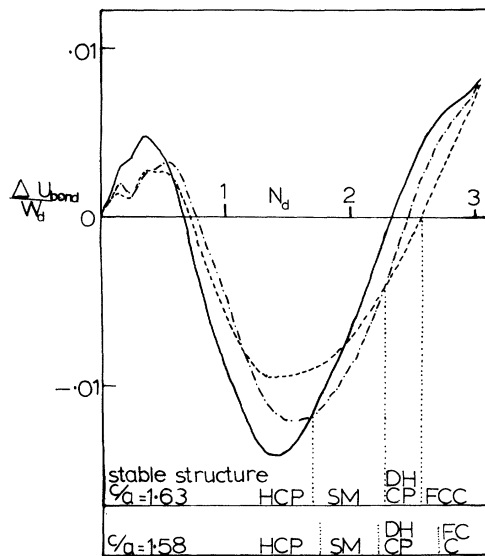
FIG. 2. The relative bonding energies of hcp- (——), dhcp- (--) and Sm-type (-·-·) with respect to the fcc structure as a function of d-band occupancy N_d. The resulting stable structures for the ideal and a nonideal axial ratio are also shown.

observed equilibrium atomic volumes. From the experimental result of the La dhcp-fcc transition[21] occurring at $V/V_0 = 0.92$ (corresponding from Fig. 1 to $\Delta N_d \simeq 0.1$), we would deduce from Fig. 2 a value of $N_d = 2.5$ for dhcp La at equilibrium. Similarly, from the results of the Lu hcp–Sm-type transition[22] occurring at $V/V_0 = 0.72$ (corresponding to $\Delta N_d \simeq 0.35$) we deduce[23] $N_d \simeq 1.5$ for hcp Lu at equilibrium. Thus, although the La results in Figs. 1 and 2 are consistent with experiment, the theoretical d-band occupancy in Fig. 1 is 0.4 electrons too large for Lu to be hcp in Fig. 2. However, we have found previously[24] that the absolute values of N_d computed by our self-consistent program are about $\frac{1}{2}$ of an electron too large for the $4d$ transition-metal series, because of the neglect of hybridization which enhances the number of states available to the s-p electrons near the bottom of the band.[25] We expect Lu to be affected by hybridization in the same way because it has a value of $C_d - B_s$ of 0.55 Ry which is very similar to that of the $4d$ metals. La, on the other hand, will experience much weaker hybridization effects because the bottom of the conduction band is pushed up with respect to the center of the d band so that $C_d - B_s$ is only 0.33 Ry. Therefore, our results for compression and change in the atomic number seem to be consistent with the experimental results.

Finally, the effect of the extra d electrons in La is also seen in the apparent deviations from the electron-per-atom rules shown by certain rare-earth Laves phases ROs_2 and RRu_2.[7,8] Johannes, Haydoch, and Heine[26] correctly predict the $MgZn_2$ structure for $LuRu_2$ and $LuOs_2$ (at $e/a = 5.7$, $G = 5$ in their Fig. 2), but the series ROs_2 has the $MgCu_2$ structure to the left of Pr, and $MgZn_2$ to the right, a similar change occurring in the RRu_2 series at G_d. Parthé[7] cites this as an anomaly in an "isoelectronic" series, but we would rather regard it as an electronic effect, the extra d electrons in La putting $LaOs_2$ above $LuOs_2$ in Fig. 2 of Ref. 26, and in fact across the phase boundary.

We are at present investigating the effect of the large core in La on other apparently anomalous properties[6] such as the large value of the superconducting transition temperature, the low melting point, and the negative coefficient of thermal expansion.

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Phase Transition in an Ising Model near the Percolation Threshold*

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The phase transition near the percolation threshold in an Ising model with random exchange is investigated. The mean-field theory of the transition is discussed. The crossover exponent φ and susceptibility are caluclated in $6 - \epsilon$ dimensions using renormalization-group methods with the result $\varphi = 1 + O(\epsilon^3)$. φ is also shown to be 1 near one dimension.

We consider an Ising model in which the nearest-neighbor exchange interaction has a probability p and $1 - p$ of taking on the values J and 0, respectively. As p is decreased the critical temperature $T_c(p)$ decreases and reaches zero at the percolation point p_c. In this Letter we study the properties of the phase transition at low temperatures and near p_c. A sketch of the phase diagram is given in Fig. 1. The two physical variables entering this problem are conveniently taken to be $r_0 \sim p_c - p$ and $w \sim e^{-2\beta J}$. The scaling fields μ_2 and μ_1 are determined by the special directions in the phase diagram in the renormalization-group sense. These directions are tangent to the critical line at p_c and along the $T = 0°$ axis, respectively.[1] Along the $T = 0°$ axis, the magnetic properties are determined by the properties of the connected spin clusters; i.e., it is a percolation problem.[2] Along the critical line away from p_c critical behavior appropriate for a random system occurs.[3] Near p_c and at low temperatures there is a competition between these two effects. Stauffer[4] and others[5,6] have argued that the point $p = p_c$, $T = 0°$ should be viewed as a multicritical point. This is discussed further be-
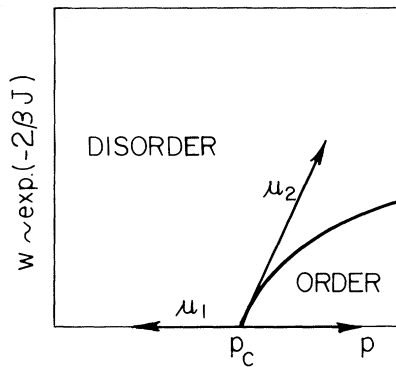

FIG. 1. Phase diagram of a random Ising model. The physical fields are $r_0 \sim p_c - p$ and $w \sim e^{-2\beta J}$. The scaling fields $\mu_2 \sim w$ and $\mu_1 \sim r_0 + aw$ are determined by the special directions.

low. A magnet with random occupation of the sites, $Rb_2Mn_pMg_{1-p}F_4$, has recently been studied experimentally near the percolation point by Birgeneau et al.[7]

In order to facilitate averaging over the quenched random exchange interaction we consider n identical replicas of the Ising model.[8] After averaging over the exchange interaction, the partition function for the n replicas is

$$Z(n) = \mathrm{Tr} \prod_{nn} \left\{ 1 + v \exp\left[\beta J \sum_{\alpha=1}^{n} (\mu_\alpha{}^i \mu_\alpha{}^j - 1)\right] \right\} \exp\left(h \sum_\alpha \mu_\alpha{}^i\right), \tag{1}$$

where $v = P/(1-p)$, $h = \beta H$, where H is the magnetic field, the Ising spin $\mu_\alpha{}^i$ on site i for replica α takes on the values ± 1, and the product is over all nearest-neighbor pairs. The required partition