

An Experimental Approach to a Simplified Band Structure of the Rare Earth Metals*

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ABSTRACT

From specific heat data it was concluded that the normal trivalent rare earth metals have a density of states at the Fermi surface of 1.5 to 2.5 states/eV/atom. Interpretation of the Hall coefficient data on the basis of a two band model suggests that the number of holes in the 6s band varies from 0.001 to 0.040. For those rare earths which have negative Hall coefficients the density of states is found to be directly proportional to the number of holes in the 6s band. The band structures of these metals is thought to consist of a nearly filled 6s band which overlaps a 5d band containing slightly more than one electron. The 4f electrons are thought to occupy discrete energy levels or very narrow one-electron bands. From these analyses Hall coefficients were predicted for terbium, holmium and scandium from the known electronic specific heat constants.

The band structures of cerium, europium and ytterbium are different from the normal rare earth metals. γ -Ce has band structure nearly like those of the normal metals, except that the one-electron 4f band lies just below the Fermi level (0.076 eV below). This low lying band explains several unusual properties of γ -Ce. α -Ce has three overlapping bands, the 6s, 5d and the narrow one-electron 4f band. The 6s band contains about two electrons, the 5d about 1 2/3 electrons and the 4f about 1/3 electron. This model accounts for the unusually high electronic specific heat constant. Europium

* Contribution No. 1461. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

and ytterbium appear to have a 6s band (containing about 1.5 electrons) which overlaps the 5d band (containing about 0.5 electron). A virtual 4f bound state model which had been proposed for cerium and ytterbium does not appear to be applicable to γ -Ce and ytterbium, but may be valid for α -Ce.

1. INTRODUCTION

A number of the physical properties from which we can obtain both direct and indirect information concerning the band structures of metals, have been measured for most of the rare earth metals. It was thought that it would be desirable to review and examine these data and try to tie them together. For this purpose the very low and room temperature heat capacities, Hall coefficients, magnetic susceptibilities, spectral data and electrical resistivities of these metals and some of their alloys were examined.

2. MAGNETIC MEASUREMENTS

The magnetic susceptibility measurements of the rare earth metals indicate directly the number of 4f electrons a particular element may have. By subtracting the number of 4f electrons from the number of electrons outside of the xenon rare gas core, one arrives at the number of electrons available for bonding, i. e. the number of valence electrons. Examination of the magnetic susceptibility data of the rare earth metals, as summarized by Aarås and Colvin [1] and Gschneidner [2], shows that all of the rare earth metals are trivalent, except for europium and ytterbium (which are divalent), and possibly cerium and samarium. A critical analysis of the magnetic behavior and other properties (metallic radii, diffuse neutron scattering values and Hall coefficients) of the cerium allotropes by Gschneidner and Smoluchowski [3] led them to conclude that the valence for both the normal face-centered cubic cerium (β) and hexa-

gonal cerium (β) is 3.05. For the collapsed face-centered cubic cerium (α) they found that the valence varies from 3.54 to 3.67 depending on the pressure and temperature. The room temperature magnetic susceptibility for samarium is in reasonable agreement with a $4f^5 5d^1 6s^2$ configuration (where the 5d and 6s electrons are the valence electrons), but the behaviors at both low and high temperatures cannot be explained by any simple model. [1, 4, 5, 6]

It should be noted that recent positron annihilation studies by Gustafson and Mackintosh [7] also confirm the trivalency of normal cerium (γ) and gadolinium, and the divalency of ytterbium.

3. VERY LOW TEMPERATURE SPECIFIC HEAT DATA

The specific heat of a metal in general is given

$$C_p = C_v^l + C_v^e + C_v^n + C_v^m + C^d \quad (1)$$

where C_p is the heat capacity at constant pressure, the subscript v designates the heat capacity at constant volume, the superscript l refers to the lattice, e the electronic, n the nuclear and m the magnetic contributions to the specific heat

TABLE I. Electronic Specific Heat Constants [9]

Rare Earth	$\gamma \times 10^4$ (cal/g-at. deg. ²)	Rare Earth	$\gamma \times 10^4$ (cal/g-at. deg. ²)
La	24.1	Tb	21.6
α -Ce	138 ^a (50.2) ^b	Dy	22.1
γ -, β -Ce	17.3 (25.1) ^b	Ho	62
Pr	52.3	Er	31
Nd	21.3 (53.7) ^c	Tm	47.1 (42.9) ^d
Pm	24	Yb	6.93
Sm	25.3	Lu	24.4
Eu	13.8 \pm 2.4 ^b	Sc	25.8
Gd	24 ^e	Y	24.1

a. This paper, see text concerning α -Ce (Section 7.2).

b. After Lounasmaa, [10].

c. After Lounasmaa, [11].

d. After Lounasmaa, [12].

e. Estimated value.

and C^d is the dilation term or the difference between C_p and C_v . C^d can be neglected for all the rare earth metals at

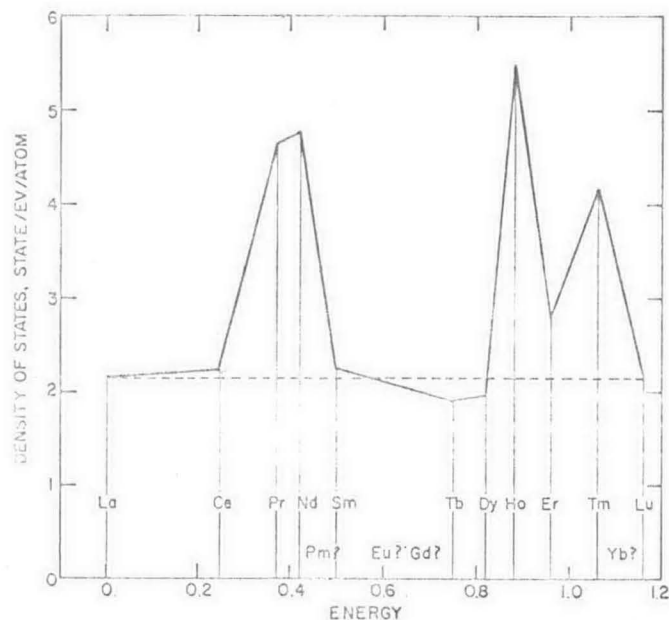


Fig. 1. Density of states values for the rare earth metals assuming that Eqn. (3) is correct and the linear contribution to the low temperature specific heat is representative of the electronic specific heat.

temperatures below 100°K , and, therefore, we can drop all subscripts in Eqn. (1). Of the terms in Eqn. (1), C^e is of prime importance here since it is directly proportional to the density of states of the electrons at the Fermi surface. The electronic contribution to the specific heat is given by

$$C^e = \gamma T \quad (2)$$

where T is the absolute temperature and γ is the electronic specific heat constant. The electronic specific heat con-

stant is related to the density of states, $N(E)$, for free electrons occupying a parabolic band by

$$N(E) = 3\gamma/2\pi^2 k^2 \quad (3)$$

where k is Boltzmann's constant. Stoner [8] has shown that Eqn. (3) is reasonably valid for any band form, except where the density of states varies rapidly with a small change in energy. The γ values for all of the elements have recently been summarized by Gschneidner [9] and are shown in Table I for the rare earth metals. Also included in Table I are some of the more recent values published by Lounasmaa [10, 11, 12] which differ considerably with the values listed by Gschneidner. [9] Examination of the γ values indicates a considerable variation as one proceeds along this series of elements, even if the values of α -Ce, Eu and Yb are excluded because they are not trivalent metals. The corresponding density of states values are shown in Fig. 1, assuming Eqn. (3) is valid. Since the outer electrons of these trivalent metals are presumably the $6s^2$ and $5d^1$, one would expect the density of states of these two bands to remain essentially constant for all the rare earth metals, as indicated by the horizontal dashed line in Fig. 1. If this is correct then the variation in the density of states must be due to the 4f electrons, which implies a broad 4f band which contains a number of peaks and valleys. (Fig. 1) The application of the rigid band model to the 4f transition metals would be expected to be valid in view of the success of this model for the d transition metals. [13, 14]. This means we could take the appropriate amounts of the two end-members, lanthanum and lutetium (ignoring crystal structure differences), and generate any of the other rare earth metals, e.g. a 13:1 atomic mixture of a La-Lu alloy (92.8 a/o La) would be equivalent to cerium, with one unpaired 4f electron, a magnetic susceptibility of about 2.4×10^{-3} emu/g-at. and a γ value of the order of 20 cal/g-at. deg². The low temperature data of Anderson, et al. [15] for some La-Lu alloys indicate absence of any appreciable

magnetic moment and the presence of superconductivity (which excludes the presence of unpaired 4f electrons [16]) in alloys containing as much as 45 at/o Lu. These results and also other measurements made on different rare earth-rare earth alloys do not suggest a common band for the 4f electrons.

Perhaps the assumption that the γ values given in Table I are representative of the electronic contribution to the specific heat is not correct. In order to deal with this possibility we shall examine the various contributions to the specific heat. The lattice contribution to the specific heat at low temperatures has a T^3 dependence, the nuclear T^{-2} dependence* and the magnetic contribution can have either a T^3 dependence for an antiferromagnetic material or a $T^{3/2}$ dependence for a ferromagnetic substance. Rewriting Eqn. (1) as

$$C_p = C_v = \gamma T + BT^3 + CT^{-2} + DT^3 + ET^{3/2} \quad (4)$$

where $D = 0$ for a ferromagnetic material, $E = 0$ for an antiferromagnetic substance, and $D = E = 0$ for a paramagnetic material. Of these contributions both the lattice and nuclear terms rest on sound theoretical grounds, but the magnetic contributions for these rare earth metals in view of their complex magnetic structures and possible Stark splitting of the ground states rest on very shaky ground. If the temperature dependence of one of four components of Eqn. (4) is incorrectly known, then the coefficients of the other terms will be incorrect. In view of the uncertainty of the magnetic contribution to the specific heats it would appear that the γ values obtained from the low temperature specific heat data of the magnetic rare earth metals are unreliable. Since trivalent lanthanum, lutetium, scandium and yttrium and divalent ytterbium are weakly paramagnetic, [2] Eqn. (4) reduces to

$$C_p = C_v = \gamma T + BT^3 \quad (5)$$

* In some instances higher order terms, such as T^{-3} , T^{-4} , etc., must also be included.

for these metals and one would expect the γ values for these five metals to be quite reliable. Indeed the mean value of γ for the four trivalent metals is 24.8×10^{-4} , with a range from 24.1×10^{-4} to 25.8×10^{-4} cal/g-at. deg².

Although this method for determining the density of states of the rare earth metals which have unpaired 4f electrons is not valid, there is, however, another method by which we can calculate the electronic specific heat constant (and thus the density of states) for these metals. This technique is described below.

4. ROOM TEMPERATURE SPECIFIC HEAT DATA

At room temperature C_v^l contribution to the specific heat is negligible since it has a T^{-2} dependence. C_v^m contributes very little or nothing to the specific heat at room temperature since these metals, except gadolinium, are paramagnetic. Thus the room temperature specific heat is given by

$$C_p = C_v^l + C_v^e + C^d + C_v^f \quad (6)$$

where the new term C_v^f is the specific heat at constant volume due to the thermal excitation of 4f electrons from the ground state to the next higher level(s) of the 4f multiplet. The specific heat due to this contribution is given by

$$C_v^f = N \frac{d}{dT} \left[\sum_J (2J+1) E_J e^{-E_J/kT} / \sum_J (2J+1) e^{-E_J/kT} \right] \quad (7)$$

where N is Avogadro's number, J the total angular momentum quantum number, E_J the energy levels of the multiplet, and k , Boltzmann's constant. For most of the natural occurring rare earth metals the C_v^f contribution at 300°K is zero and can be ignored. But for cerium, praseodymium, neodymium, samarium and terbium the C_v^f contribution at 300°K is not zero and must be included in our analysis. The C_v^f contribu-

tion for these five metals was calculated by using Eqn. (7) and was found to be 0.01 cal/g-at. deg. for cerium, praseodymium and terbium, 0.02 for neodymium and 0.46 for samarium.

TABLE II. Coefficients of Thermal Expansion, Atomic Volumes and Compressibilities Used to Calculate C [9]

Rare Earth	Coefficient of Expansion $\alpha \times 10^6$ ($^{\circ}\text{C}^{-1}$)	Atomic Volume ($\text{cm}^3/\text{g-at.}$)	Compressibility $\beta \times 10^7$ (cm^2/kg)
γ -Ce	8.5	20.69	40.97
Pr	6.79	20.82	32.08
Nd	9.98	20.59	30.02
Sm	10.4	19.95	33.36
Eu	33.1	28.98	66.63
Gd	6.28	19.94	25.59
Tb	10.3	19.26	24.6
Dy	10.0	18.99	25.52
Ho	10.7	18.75	24.72
Er	12.3	18.46	23.88
Tm	13.3	18.13	24.71

The dilation term is given by

$$C^d = \frac{9\alpha^2 TV}{\beta} \quad (8)$$

where α is the linear coefficient of thermal expansion, V the atomic volume and β the isothermal compressibility. The values of α , V and β which were used in Eqn. (8) to calculate C^d are listed in Table II.

From the Debye theory of the lattice specific heat we have the following expression for C_V^l :

$$C_V^l = 3R [K(y) - yK'(y)] \quad (9)$$

where R is the gas constant, $y = \theta/T$ (θ is the Debye temper-

ature and $K(y)$ is given by

$$K(y) = \frac{3}{y^3} \int_0^y \frac{y^3 dy}{e^y - 1} \quad (10)$$

TABLE III. Debye Temperatures Used to Calculate C_V^l [9]

Rare Earth	Debye Temperature ^a ($^{\circ}\text{K}$)
γ -Ce	138
Pr	138
Nd	148
Sm	148
Eu	121 ^b
Gd	155
Tb	158
Dy	158
Ho	161
Er	163
Tm	167

a. Based on specific heat data taken from about 15 $^{\circ}$ to 300 $^{\circ}\text{K}$.

b. Calculated by ref. [9] from Lindemann equation.

The integral in Eqn. (10) has been solved, and tables of C_V^l vs θ/T may be found in a number of sources* (of these, we have used the tables of Lewis *et al.* [16a] to determine C_V^l at 300 $^{\circ}\text{K}$). The Debye temperature used to calculate C_V^l are listed in Table III.

After these three contributions to specific heat were calculated, they were added together and subtracted from C_p to give C_V^e . The values for the various contributions to the specific heat are summarized in Table IV along with the resultant C_V^e term and the electronic specific heat constant, γ .

* Some of these sources are listed in the compilation by Gschneidner. [9].

TABLE IV. The Calculated C_v^1 , C_v^2 and C^d and Contributions to the Specific Heat, the Measure C_p Values, and Resultant C_v^e and γ Values (all values in cal/g-at. deg. units, except for γ values which are in cal/g-at. deg.² units)

Rare Earth	C_v^1	C_v^2	C^d	C_p	C_v^e	$\gamma \times 10^4$
γ -Ce	5.898	0.010	0.023	6.47 ^a	0.539	18.0
Pr	5.898	0.010	0.019	6.45 ^b	0.523	17.4
Nd	5.889	0.020	0.043	6.55 ^a	0.616	20.5
Sm	5.389	0.460	0.039	6.80 ^a	0.826	27.5
Eu	5.913	-	0.302	6.48 ^b	0.265	8.83
Gd	5.382	-	0.019	6.561 ^c	0.660	22.0
Tb	5.879	0.010	0.051	6.812 ^d	0.872	29.1
Dy	5.879	-	0.045	6.577 ^e	0.353	21.8
Ho	5.875	-	0.055	6.498 ^f	0.508	18.9
Er	5.873	-	0.073	6.718 ^g	0.772	25.7
Tm	5.866	-	0.082	6.460 ^h	0.512	17.1

a. After Spedding, McKeown and Daane, [17].

b. After Berg, Spedding and Daane, [18].

c. After Dennison, [19].

d. Because of a small magnetic contribution to C_p at 300°K, the C_p values at 320°, 340° and 360°K given by Jennings, Stanton and Spedding [20] were extrapolated to 300°K to give this value.

e. Mean value from data of Dennison [19] and Griffel, Skochdopole and Spedding (ref. 21).

f. After Gerstein, et al., [22].

g. After Skochdopole, Griffel and Spedding, [23].

h. After Jennings, Hill and Spedding, [24].

The mean value of γ for the ten trivalent metals is 21.8 which is in reasonable agreement with the low temperature values of lanthanum and lutetium (24.1 and 24.4, respectively). Although the values in Table IV vary from 17.1 to 29.1 they should be considered to be approximately constant in view of the assumptions involved in this calculation. These results indicate that the large values of γ obtained from low temperature specific heat measurements for praseodymium, neodymium, holmium, thulium and probably erbium are incorrect and should be substantially lower. The γ values given in Table IV also support a band model which consists of overlapping 6s and 5d bands containing three electrons and the absence of an overlapping 4f band.

The γ value calculated by this technique for europium is in reasonable agreement with that of ytterbium, (see Table I) considering the Debye temperature used in the calculations was obtained from the Lindemann relationship. The γ value for europium, however, is approximately 50 per cent smaller than the value obtained from very low temperature specific

heat data. (See Tables I and IV) But as for the other rare earth metals which have unpaired 4f electrons, there are both nuclear and magnetic contributions to the low temperature specific heat which make it difficult to evaluate the electronic contribution. It is felt that the value obtained from the room temperature specific heat data is the more reliable γ value.

5. HALL COEFFICIENTS

Hall coefficients, which have been measured for most of the rare earth metals by Kevane, *et al.* [25] and Anderson, *et al.* [26] could not be interpreted on the basis of a simple one band model. [25, 26] Kevane, *et al.* [25], however, were able to reasonably explain their results in terms of the two band model proposed by Sondheimer. [27] Sondheimer showed that the relationship between the Hall coefficient, R_H , and the balance between the number of electrons in the d band, n_d , and the holes in the s band, n_s , taking part in conduction is given by

$$R_H = \frac{1}{Ne} \frac{n_s - n_d \left(\frac{\mu_d}{\mu_s} \right)^2}{\left[n_s - n_d \left(\frac{\mu_d}{\mu_s} \right) \right]^2} \quad (11)$$

where N is the number of atoms per unit volume, e the electronic charge, μ_s and μ_d are the respective mobilities in the s and d bands. The relationship between n_d and n_s is

$$n_d = v - 2 + n_s \quad (12)$$

where v is the valence. By substituting Eqn. (12), the values of N and e and the experimental value of R_H into Eqn. (11) we get a relationship between (μ_d / μ_s) and n_s , which is graphically illustrated in Fig. 2 for most of the metals. Kevane *et al.* [25] noted that if ratio of the mobilities of the

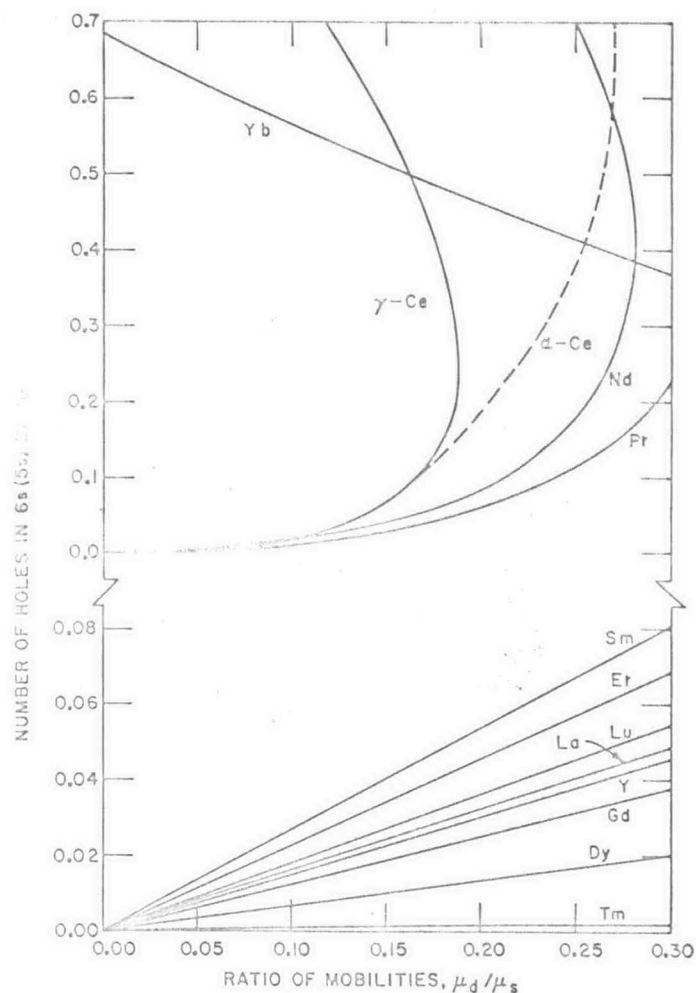


Fig. 2. Relationship between the ratio of the mobilities and the number of holes in the s band of some of the rare earth metals as determined from the measured Hall coefficients.

d electrons to the s electrons was 0.1 or less, then the observed Hall coefficients, which differed both in magnitude

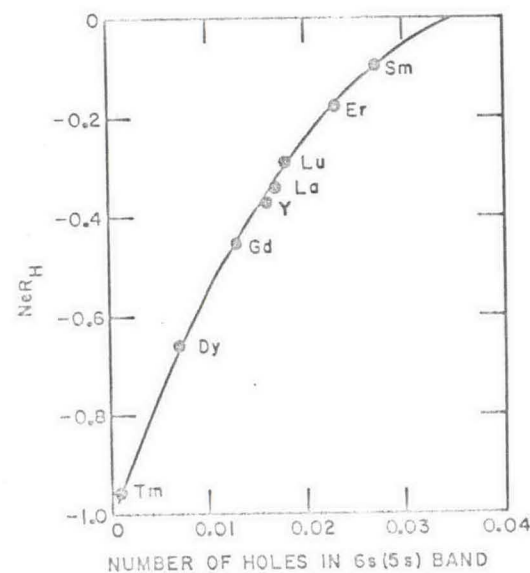


Fig. 3. The atomic Hall coefficient per unit volume, NeR_H , vs the number of holes in the s band for a mobility ratio of 0.1.

and sign, could be accounted for by small changes in the number of holes in the s band for lanthanum, cerium, praseodymium, neodymium, gadolinium, dysprosium, erbium and yttrium. In all cases the 6s (5s for yttrium) band was nearly full and the 5d (4d for yttrium) band contained slightly more than one electron. Gschneidner and Smoluchowski [3] re-examined the Hall coefficient data for cerium using the same model and concluded that the number of holes in the 6s band and electrons in the 5d band is insensitive to the choice of valence between 3 and 4 for either γ or α -Ce. If the data of Anderson, *et al.* [26] for samarium, thulium, yttrium and lutetium are analyzed in terms of the Sondheimer [27] model (noting that yttrium has only 2 valence electrons) a conclusion similar to the drawn by Kevane *et al.* is made for

samarium, thulium and lutetium (Fig. 2). For ytterbium the Hall coefficient indicates 0.56 holes in the 6s band and this number of electrons in the 5d band, assuming the ratio of the mobilities to be 0.1.

The relationship between the Hall coefficient (or more precisely the atomic Hall coefficient per unit volume, NeR_H) and the number of holes in the 6s (5s for yttrium) band for a mobility ratio of 0.1 is shown in Fig. 3 for those rare earth metals which have negative Hall coefficients. This behavior is not at all unreasonable, in view of the positions of the almost straight lines shown in the bottom of Fig. 2. That is, the larger (more negative) the Hall coefficient the smaller the number of positive carriers (holes) in the 6s (or 5s) band.

6. BAND* STRUCTURE OF THE NORMAL TRIVALENT RARE EARTH METALS

From the above data it should be possible to construct a simple band structure for the rare earth metals. The Hall coefficient data suggest that the 6s band has approximately 0.01 hole, and the electronic specific heat constant data suggest a density of states of about 2.0 states/eV/atom at the Fermi surface. A closer examination of these data (Fig. 4) show that the density of states increases as the number of holes in the 6s band (and as the number of electrons in the 5d band) increase. This is what one might expect, but the agreement shown in Fig. 4 is much better than one could possibly hope for, considering the assumptions made in determining the density of states values especially for magnetic rare earth metals and in applying Sondheimer two band model to obtain the number of holes in the s band. It is also interesting to note that there is no regular or systematic variation of the density of states or the number of holes in the s band for these metals, as is observed for most of the physical

* When we talk about a particular type band, such as the 6s, we really mean a band which has s-like character.

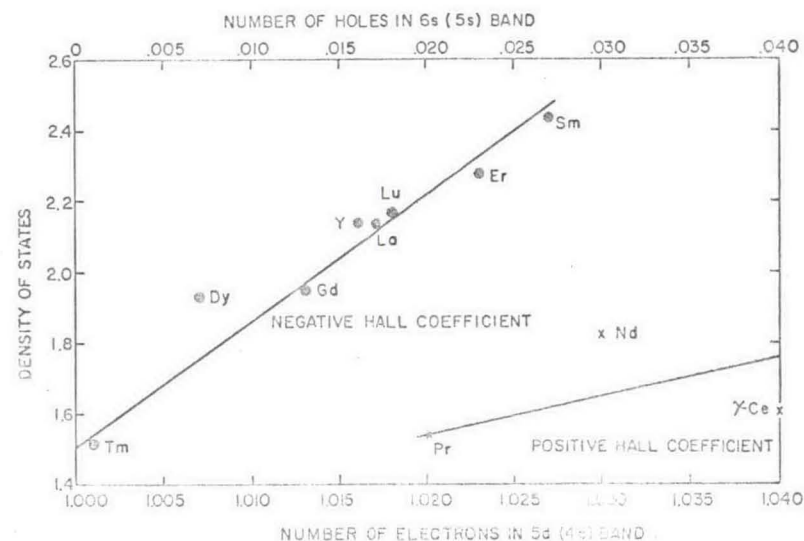


Fig. 4. The density of states at the Fermi level vs the number of holes in the s band (number of electrons in the d band).

properties of these metals. Nor does there seem to be any dependence on the spin, or the projection of the spin on the lowest J state, or the orbital angular quantum number, or the total angular quantum number.

From the data shown in Fig. 4, the band structures of three representative rare earth metals, which have negative Hall coefficients, are shown in Fig. 5. Thulium, which has the lowest density of states, has the smallest number of holes in the 6s band, and samarium, which has the largest density of states, has the largest number of holes in this band. The other metals, which have density of states values which are intermediate between these two extremes, have band structures represented more or less by gadolinium. It is noted that, if the band structures shown in Fig. 5 are correct, then

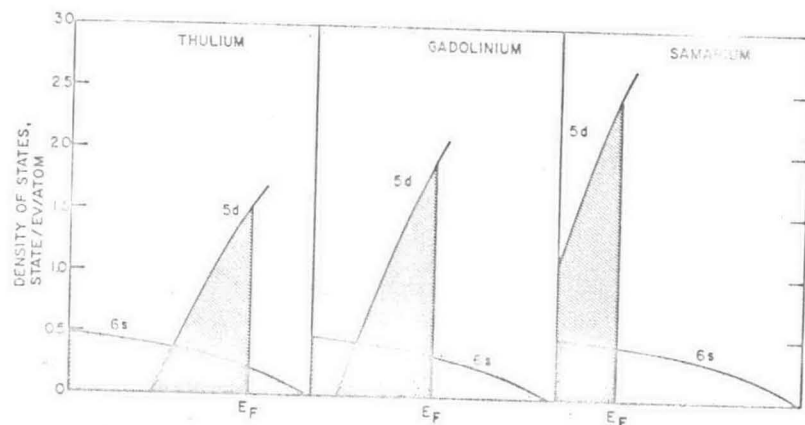


Fig. 5. The simplified band structures of three of the rare earth metals which have negative Hall coefficients.

the relative positions of the 6s and 5d bands with respect to each other must shift from one element to another. Furthermore, it is concluded that there is no broad 4f band which overlaps the 6s and 5d bands; most likely, the 4f electrons occupy discrete levels, or very narrow one electron bands as proposed by Mott. [28]

For the rare earth metals, which have positive Hall coefficients, the density of states are significantly smaller for a corresponding number of holes in the 6s band (Fig. 4). Thus one would expect the band structures of praseodymium and neodymium to be slightly different from those shown in Fig. 5, but the general conclusions mentioned above for the metals which have negative Hall coefficients are expected to apply to praseodymium and neodymium. Discussion of the band structure of γ -Ce is deferred to section 7.1.

The band structures proposed here for the rare earth metals are in general agreement with the conclusions arrived at by Rocher [29] in his analysis of the electronic and magnetic properties of these metals, except for the metals cerium and ytterbium, which will be discussed later.

6.1 α - and β - LANTHANUM.

Lanthanum at room temperature generally consists of a mixture of two allotropes, face-centered cubic (β -La) and hexagonal (α -La), unless special precautions are taken to obtain one or the other allotrope. The α - β transformation occurs on heating at about 580°K (310°C) and on cooling at about 490°K (220°C). The transformation on cooling $\beta \rightarrow \alpha$ is sluggish and very seldom goes to completion. All of the experimental data, which were analyzed to determine the band structure of lanthanum, are from samples which contain both phases. Thus it is impossible to know the correct value of the density of states of either α or β -La. It is, however, possible to determine the density of states of α -La relative to β -La. This is outlined below.

Suhl and Matthias [30] have given a relationship between the density of states and the superconducting transition temperature, T_s , for a superconductor (*e.g.* lanthanum) containing some paramagnetic impurity atoms (*e.g.* gadolinium). Rewriting their Eqn. (29) as:

$$\frac{dT_s}{dc} = -\frac{\pi^2}{7} J^2 S(S+1) \frac{N(E)}{k} \quad (13)$$

where c is the concentration of the paramagnetic impurity in a/o, J the exchange energy of the spin coupling between a paramagnetic ion and a conduction electron, S the spin of the paramagnetic ion and k the Boltzmann constant. Since J is quite difficult to evaluate, only an order of magnitude value can be obtained for $N(E)$. But for lanthanum the value of dT_s/dc is known for gadolinium impurities in both α and β -La. If we make the reasonable assumption that J is identical for these two cases, then we see that the term $(\pi^2/7k)J^2 S(S+1)$ is a constant, and that

$$\frac{N(E)_\alpha}{N(E)_\beta} = \left(\frac{dT_s}{dc} \right)_\alpha / \left(\frac{dT_s}{dc} \right)_\beta \quad (14)$$

where the subscripts α and β designate α -La and β -La respectively. The value of $(dT_s/dc)_\alpha$ is -4.5°K per 1 a/o [31] and $(dT_s/dc)_\beta$ is -5.1°K per 1 a/o [16]. Substituting these values into Eqn. (14) we find $N(E)_\beta = 1.13N(E)_\alpha$, or in other words the density of states of β -La (face-centered cubic) is 13 per cent larger than that of α -La (hexagonal).

6.2 PREDICTION OF HALL COEFFICIENTS.

The Hall coefficients of terbium, holmium and scandium have not been measured, however, it is possible to estimate these values from their measured electronic specific heat constants, γ . If the density of states, $N(E)$, is calculated from γ by using Eqn. (3), we can determine the number of holes in the s band from Fig. 4, which in turn can be used to find N_eR_H from Fig. 3. Once N_eR_H is known it is a simple matter of calculating the Hall coefficient, R_H . The predicted values of the Hall coefficients (in units of volt-cm/amp-Oe) are:

Tb	-0.11×10^{-12}
Ho	-1.5×10^{-12}
Sc	-0.32×10^{-12}

It is interesting to note that as the final pages of this paper were being written an abstract [32] of a Russian publication on some transport and magnetic properties of scandium became available. This abstract [32] noted that scandium has a Hall coefficient of -0.30×10^{-12} , which is in very good agreement with the predicted value.

In a similar manner the Hall coefficient of β -La with respect to that of α -La can be estimated from the result shown earlier that $N(E)_\beta = 1.13 N(E)_\alpha$. It is found that $(R_H)_\beta \approx 0.4 (R_H)_\alpha$, and since a sample containing a mixture of both α and β -La phases had a R_H value of -0.8×10^{-12} , it is obvious that the Hall coefficient of β -La will be less negative than that of α -La.

7. BAND STRUCTURE OF CERIUM

Cerium metal has four allotropic modifications, two are face-centered cubic, one body-centered cubic and one hexagonal. The normal room temperature face-centered cubic form, γ -Ce, and the hexagonal form, β -Ce, have been suggested to have a valence of 3.05 [3] and presumably the high temperature body-centered cubic δ -Ce has also a similar valence. At low temperatures ($\sim 120^\circ\text{K}$ and 1 atm) or at high pressure (~ 7.5 kb and 298°K) γ -Ce form transforms to the second face-centered cubic modification, α -Ce, with a large contraction in volume (17 to 12 per cent depending on pressure and temperature). This large volume change has been suggested by many to be due to the transfer of the 4f electron in cerium to the 5d band (see ref. 3 for a complete review of the pertinent literature). Gschneidner and Smoluchowski [3] have concluded from their examination of the physical properties of cerium and cerium-rich alloys that the valence of α -Ce is 3.67 at 1 atm and 116°K . Also in support of this valence for α -Ce are the calculations of Waber *et al.* [33]. If these values are correct or nearly so, we may ask ourselves what is the band picture for α - and γ -Ce?

7.1 γ -CERIUM.

In order to explain the valence of 3.06 for γ -Ce one might suggest that there is a 4f one electron band which overlaps the 6s and 5d bands near the Fermi energy, such that about 0.06 of a hole exists in the 4f band and that the magnitude of the density of states is still governed by the 5d level. The order of magnitude of most of the observed physical properties of the cerium does not rule out this model. It is difficult to determine the sign and order of magnitude of the Hall coefficient on the basis of three overlapping bands since no mathematical solution has been proposed for this model. Infrared studies of γ -Ce at 298°K by Wilkins, *et al.* [34] revealed a large absorption at 15.5 microns, which they have not explained, and a number of minor peaks at shorter wave

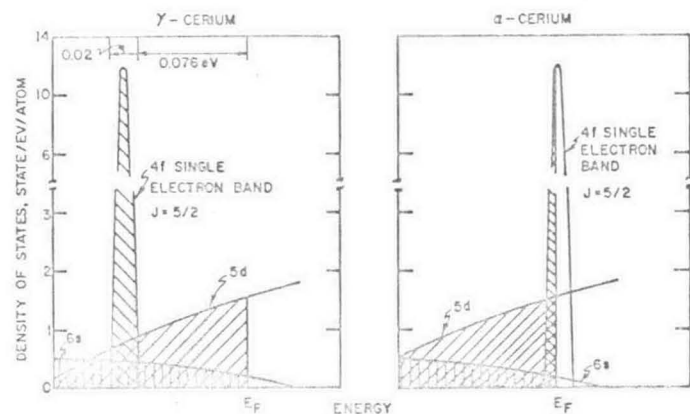


Fig. 6. Band structure of γ -Ce (a) and α -Ce (b).

lengths, which are probably due to intra-atomic transitions from the $J = 5/2$ (ground state) multiplet to the $J = 7/2$ multiplet. [35] The above model for cerium, however, is not capable of explaining this 15.5μ absorption peak.

A model which is capable of explaining this and most of the observed physical properties is shown in Fig. 6a. The 15.5μ absorption would be due to the excitation of electrons from the narrow 4f single electron band to the 5d or 6s band at the Fermi level. The wavelength at which this transition occurs, suggests that the 4f level lies 0.076 eV below the Fermi energy and the width of the transition suggests that the one electron 4f band is very narrow, about 0.02 eV wide. The height of the 4f band is not known, but it is assumed to be higher than the density of states value obtained from the electronic specific heat constant of α -Ce (see Section 7.2). The Boltzmann distribution ($\exp \Delta E/kT$) indicates that at room temperature 0.05 electrons are thermally excited to the 5d 6s band. This means that γ -Ce has an effective valence of 3.05, which is in very good agreement (better than one might expect) with the valence proposed by Gschneidner and Smoluchowski [3]. Since these authors based their valence on the magnetic properties and the atomic size of γ -Ce, these properties fit this model. Furthermore, since the

height of the 5d band at the Fermi level and the number of holes in the 6s band were derived from the specific heat and the Hall coefficient data, respectively, these properties naturally are in agreement with this model.

Rocher [29] suggested that a virtual 4f bound state model could explain the behavior of cerium (presumably γ -Ce) at high temperatures. In order to explain the high resistivity and the magnetic susceptibilities of cerium he proposed that cerium had a very large density of states (implying a partially occupied 4f band), which he believed was confirmed by the low temperature specific heat data of Parkinson and Roberts. [36] This, however, leads to two difficulties: (1) the low temperature specific heat data which yield a large γ value are appropriate for α -Ce and not γ -Ce* and (2) the large value of γ gives a C_V^e contribution at 300°K of 1.26 cal/g-at. deg and leads to a Debye temperature of 500°K , which is a factor of two to three times larger than those of any of the other rare earth metals. Furthermore, this model does not explain the large infrared absorption at 15.5μ . For these reasons it is felt that the virtual 4f bound state model does not apply to γ -Ce, however, it may be a valid model for α -Ce (see below).

Rocher [29] also pointed out that a large value of the density of states is required to explain the magnetic contribution to the resistivity and the high temperature magnetic susceptibility of γ -Ce. If this is correct, then this casts some doubt on the validity of the band model proposed herein for γ -Ce.

Rocher [29] gives a value of $70 \mu \text{ ohm-cm}$ for magnetic resistivity of cerium. This value is unreasonably large. Recent resistivity values for lanthanum vary from 57 to $80 \mu \text{ ohm-cm}$ [38, 39, 40] and for cerium from about 75 to $85 \mu \text{ ohm-cm}$ [38, 39]. If cerium had a magnetic resistivity of about $70 \mu \text{ ohm-cm}$ as suggested by Rocher, we would expect cerium to have a room temperature resistivity of 125 to $150 \mu \text{ ohm-cm}$ (i.e. about $70 \mu \text{ ohm-cm}$ larger than that of lan-

* At temperatures below 100°K all of the γ -Ce has transformed to α -Ce. [37]

thanum). Furthermore, since the residual resistivities of most of the rare earth metals are about 5μ ohm-cm, then for cerium almost all of the room temperature resistivity can be accounted for by only the residual and magnetic resistivities (i. e. $5 + 70 = 75 \mu$ ohm-cm). For the rare earth metals the thermal contribution to the resistivity is of the order of 50μ ohm-cm. Thus, it appears that the magnetic contribution to the resistivity of cerium is much less than 70μ ohm-cm. It is probably of the order of 5 to 20μ ohm-cm, which is in as good agreement as many of the other rare earth metals (see Table 5, p. 245 of Rocher's article in *Advances in Physics*, ref. 29).

In order to explain the high temperature magnetic susceptibility Rocher [29] used a modified form of the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta_p} + \chi_p \quad (15)$$

where the χ values are the gram susceptibilities, C is the Curie-Weiss constant, θ_p the interaction temperature and χ_p the temperature independent Pauli contribution to the magnetic susceptibility. Rocher was able to explain the high temperature magnetic susceptibility by using values of -45°K for θ_p , 2×10^{-6} emu/gm for χ_p , 2.40 Bohr magnetons for the magnetic moment (which is equal to $2.83 \sqrt{CM}$, where M is the atomic weight), and 2500 cm^{-1} for the separation of the $J = 5/2$ and $J = 7/2$ levels of the 2F_7 multiplet of cerium. Since the Pauli contribution to the susceptibility (which is also directly proportional to the density of states) is about 2 1/2 times larger than that of lanthanum, Rocher concluded that cerium has a high density of states. However, magnetic susceptibility data are not sensitive enough to determine χ_p very accurately. Arajs and Colvin [1] have also analyzed the high temperature magnetic susceptibility of cerium and they obtained the following constants: $\theta_p = -50^\circ\text{K}$, $\chi_p = 1.00 \times 10^{-6}$ emu/gm, $\mu_B = 2.52$ Bohr magnetons and 2129 cm^{-1} for the separation of levels in the 2F_7 multiplet. Furthermore,

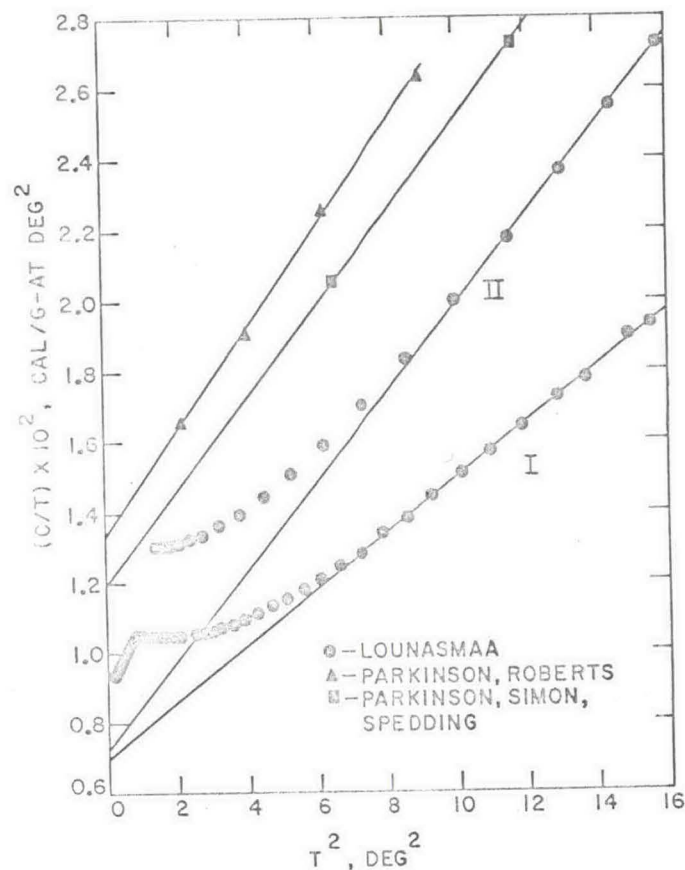


Fig. 7. Plot of C/T vs T^2 of the very low temperature specific heat of cerium. Although only two of Parkinson's, Simon's and Spedding's data points are shown in this plot, additional values at higher temperatures indicate that the straight line passes through these two points as drawn. Lounasmaa's data were taken on two samples containing different amounts of α and β -Ce.

they state: "It has been found that, besides the 4f-electron contribution to the total paramagnetism of any one of the rare

earth metals--except, possibly, europium--a small, approximately temperature-independent paramagnetic susceptibility of magnitude $1 \times 10^{-6} \text{ g}^{-1} \text{ cm}^2$ [*sic*, same as emu/gm] exists, and this originates from the conduction electrons."

From this it is seen that the magnetic susceptibility data of γ -Ce do not require the density of states of γ -Ce to be any larger than those of other rare earth metals.

From the above discussion it is concluded that the experimental resistivity and magnetic susceptibility data are consistent with the band structure proposed herein for γ -Ce as shown in Fig. 6a.

7.2 α -CERIUM.

The non-integral value proposed for the valence of α -Ce [3] suggests that about 60 per cent of the 4f electrons no longer occupy the one electron 4f band and are probably in the 5d band. A band structure which would take this into account is shown in Fig. 6b. In this model one would expect high density of states (much larger than 2.0 states/eV/atom) since the Fermi level would lie slightly below the middle of the 4f band. An examination and an analysis of the published low temperature specific heat data indicates that the density of states is indeed very large. (Fig. 7) At low temperatures ($< 100^\circ\text{K}$) cerium consists of a mixture of α and β phases. Because of this, γ values, which were obtained as the intercepts of the straight lines in Fig. 7, were assumed to be equal to the weighted sum of the γ value of each phase, i. e.:

$$\gamma = w_\alpha \gamma_\alpha + (1 - w_\alpha) \gamma_\beta \quad (16)$$

where w_α is the fraction of α in the sample. The electronic specific heat constant of β -Ce (γ_β) was assumed to be 18 cal/g-at. deg², the same as that of γ -Ce. The data of Parkinson *et al.* [41] yield a value of 131×10^{-4} cal/g-at. deg² for the electronic specific heat constant of α -Ce; the data of Parkinson and Roberts [36] for their sample which had been cycled 50 times yield 200×10^{-4} ; and the data of

Lounasmaa [10] yield a mean value of 138×10^{-4} for his samples I and II. The amounts of α and β -Ce present in the first two investigators' samples were not known and were estimated on the basis of the results of Gschneidner, *et al.* [37]. From X-ray measurements Lounasmaa, however, did give estimates of the amounts of α and β -Ce present in his sample, and therefore, we feel that his value for the electronic constant of α -Ce is the best available. By using Eqn. (3) a value of $\gamma = 138 \times 10^{-4}$ yields a density of states of 12.2 states/eV/atom at the Fermi level of the 1/3 filled 4f one-electron band of α -Ce. It is assumed since the band is only 1/3 filled that the top of this band is greater than 12.2.

Although there is a large variation in the γ values estimated in the above manner, the important thing is that they are all extremely large. This variation may be due, not only to the approximations involved in estimating the quantities of α and β -Ce in the samples, but also to impurities which may change the electron concentration and thus the Fermi level. Any small change in the Fermi level would be expected to cause a large change in the density of states because of the narrowness of the 4f band.

With such a narrow band the high density of states of α -Ce should be very sensitive to temperature and to impurities. Indeed by using the method of Mott [42], the degeneracy temperature of this band is calculated to be 116°K . Alloying studies would be very revealing if one could prevent the β -Ce from forming upon cooling. Indeed it would be desirable if one could obtain pure α -Ce to measure the physical properties of it at low temperatures.

When γ -Ce transforms to α -Ce it not only undergoes a large volume contraction, but also a large decrease in the electrical resistivity (from $70 \mu \text{ ohm-cm}$ to $30 \mu \text{ ohm-cm}$). This decrease in resistivity can be crudely accounted for by the increase in the number of conduction electrons (by about 2/3 of an electron per atom) and the decrease in the number of 4f electrons (by about 2/3 of an electron per atom), which give rise to the magnetic contribution to the resistivity. Interband scattering (s-f and d-f) would be expected to cause

an increase in the resistivity of α -Ce (this contribution is zero in γ -Ce because the 4f level is essentially filled). We can roughly estimate the decrease in the resistivity of the first two contributions mentioned above. The resistivity of the tetravalent metals titanium, zirconium, hafnium and thorium range from 18 to 43 μ ohm-cm. [43] Assuming a mean value of 60 μ ohm-cm for a normal trivalent rare earth metal with no 4f electrons*, and a mean value of 30 μ ohm-cm for the tetravalent metals, we would expect a decrease in resistivity of 30 μ ohm-cm for a metal which has undergone a valence change from three to four. The magnetic contribution to resistivity of a metal with one 4f electron is about 6 μ ohm-cm [44]. Since in the case of the cerium transformation about 2/3 of the 4f electron goes into the 5d 6s band, we would expect a resistivity decrease of about 25 μ ohm-cm (2/3 times 30 + 6). This is somewhat smaller than the 40 μ ohm-cm change observed, but it is still about the right order of magnitude to account for this change considering the approximations made. From this it would appear that the s-f and d-f interband scattering contribution to the resistivity is quite low and perhaps negligible.

It should be noted that Rocher's virtual 4f bound state model [29] appears to apply to α -Ce, and it may be considered to be an alternate approach to the understanding of the behavior of this phase.

8. BAND STRUCTURE OF EUROPIUM AND YTTERBIUM

8.1 EUROPIUM

Europium has only two valence electrons available. These two electrons could easily fill the 6s band, and if there were no overlapping 5d band europium would either be a semiconductor or an insulator and the density of states would be zero.

* Resistivities of scandium, yttrium and lanthanum vary from 57 to 67 μ ohm-cm.

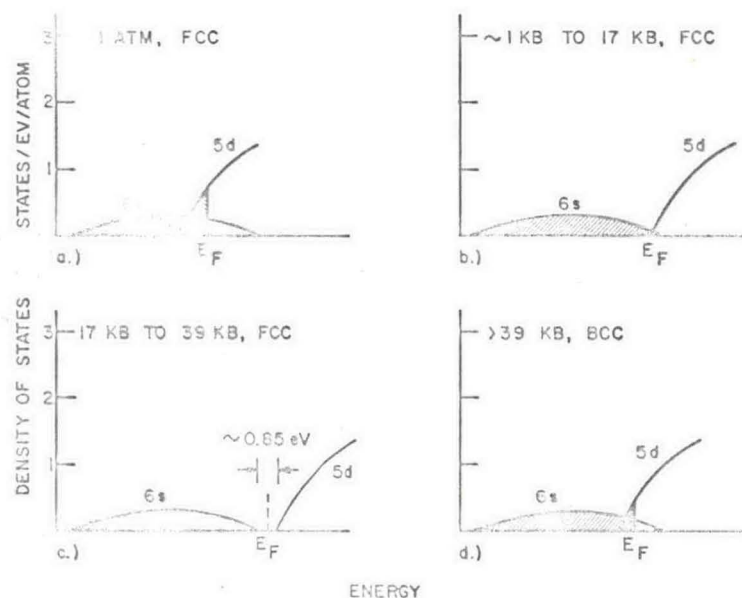


Fig. 8. Band structure of ytterbium as a function of pressure at constant temperature.

But since europium is a good conductor and it has appreciable electronic specific heat constant, there must be an overlapping 5d level. The magnitude of the electronic specific heat constant (8.83) suggests that the density of states is governed by the Fermi level in the 5d band rather than the 6s band.* In all probability there are about 1.5 electrons in the 6s band and 0.5 in the 5d band, very much like the band structure of ytterbium which is shown in Fig. 8a (ignoring the differences in the crystal structures of these two metals). Hall coefficient measurements on europium would be extremely useful.

* In metals, which are thought to have only s-bands, the electronic specific heat constant has never been found to be greater than 3.0×10^{-4} cal/g-at. deg² (see data given in ref. 1).

8.2 YTTERBIUM.

The electronic specific heat constant and Hall coefficient for ytterbium suggest the band structure shown in Fig. 8a, where the density of states at the Fermi level is 0.78 states/eV/atom and the 5d band has 0.56 electrons (and conversely the 6s band has 0.56 holes).

Bridgman [45], Stager and Drickamer [46], Hall and Merrill [47] and Souers and Jura [48] have found that as pressure is applied ytterbium slowly changes from a good conductor to a poor conductor to a semiconductor, and finally at 39 kb it abruptly changes back to a good conductor. The proposed band structures for these behaviors is shown in Figs. 8a through 8d. The band structure of face-centered cubic ytterbium at atmospheric pressure is shown in Fig. 8a. As pressure is applied the bands shift with respect to each other as is shown in Fig. 8b. Then as more pressure is applied the bands continue to shift and finally a gap is formed between the completely filled 6s and the empty 5d band (Fig. 8c) giving rise to the semiconducting properties of ytterbium. The energy gap, as measured on impure (as semiconductors are concerned) ytterbium by Souers and Jura [48], is about 0.85 eV. As the pressure is increased to 39 kb, the resistance suddenly decreases by a factor 10 to 13 and ytterbium is now a better conductor than it was at atmospheric pressure. Hall's and Merrill's data [47] show that face-centered cubic ytterbium transforms to body-centered cubic ytterbium at this pressure, with about a change in the metallic radius from 1.81 to 1.74Å. McWhan and Jayaraman [49] have shown that this change in the metallic radii is almost entirely accounted for by the change in coordination (the discrepancy of 0.01Å can easily be accounted for by experimental error). On the basis of this evidence we suggest that the band structure of body-centered cubic ytterbium at pressures greater than 39 kb is similar to that shown in Fig. 8d. Hall coefficients and possibly magnetic susceptibility measurements of high pressures would be extremely useful in confirming this model.

Rocher [29] suggested that the 39 kb transformation* in ytterbium was due to the transition of about one half of a 4f electron per atom to the valence band. He was able to correlate the data, which were available at that time, in terms of a virtual 4f bound state model with a partially occupied one electron 4f level. More recent X-ray studies of Hall and Merrill [47] and the subsequent interpretation of their atomic size data by McWhan and Jayaraman [49] have shown that ytterbium undergoes a crystal structure change, but no valence change at 39 kb. Because of this it would appear that the virtual 4f bound state model is not applicable to ytterbium at high pressures.

9. CONCLUSION

The above band models proposed for the rare earth metals are greatly simplified and it is amazing that the high temperature specific heat and Hall coefficient data give such consistent results. The biggest disappointment is that very low temperature specific heat data, except for the non-magnetic metals, do not seem to yield any reliable data concerning the band structures of these metals.

Before very high purity rare earth metals (99.99+ a/o pure with respect to all impurities) become available to make direct Fermi surface measurements, there are a number of careful experiments that can be performed on these metals, which should give us some reliable data on their band structure. Low temperature elastic constant measurements on single crystals would yield an independent method for determining the Debye temperature and thus the lattice contribution to the specific heat. Specific heat measurements at very

* Rocher used 65 kb for this transition in his paper. This larger value is taken from Bridgman [45], which was the only value available to Rocher at that time. Bridgman's transition pressure is high because (1) his ytterbium was probably not as pure as that available to later investigators [46, 47, and 48], and (2) his pressure scale was too high compared to the presently acceptable pressure scale.

low temperatures on even-even rare earth isotopes (thus eliminating nuclear contributions to the specific heat) and at very high magnetic fields of the order of 100,000 to 1,000,000 gauss (which would hopefully saturate the magnetic spins and eliminate the magnetic contribution to the specific heat) would be quite informative. This latter experiment, however, might be quite difficult to achieve in the near future. Hall coefficient measurements on the remaining rare earth metals need to be made to complete the picture. Extension of Hall coefficient measurements to all the metals at high pressures would also be very interesting. Spectral studies of these metals would also be desirable to see if any other transitions similar to cerium exist.*

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* Tannhäuser [50] examined the visible light-spectra of thin films of praseodymium, neodymium, samarium and erbium. He found only a broad absorption, which he concluded was due to the interaction of 4f electrons with the conduction electrons.

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