

On the Compressibility of Metallic Cesium*

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(Received November 1, 1949)

The volume discontinuity of cesium at 45,000 kg/cm² is attributed to a shift of the valence electrons from the 6s zone to the empty 5d zones. A Wigner-Seitz calculation for the 6s and 5d bands supports this explanation. The potential used is described and tabulated. The possible existence of similar transitions for potassium and rubidium is discussed.

I. INTRODUCTION

IN investigating the compressibility of cesium, Bridgman¹ found a volume discontinuity of 11 percent at 45,000 kg/cm². Above the transition the compressibility is unexpectedly small in comparison with the other alkalis and decreases abnormally rapidly with increasing pressure. Figure 1 shows the volume as a function of the pressure.

In order to explain the phase transition, Fermi proposed that the valence electron is forced into a vacant internal orbit. This hypothesis is suggested by the large volume change and the proximity of cesium to the rare earths. The two available orbits are 4f and 5d. The possibility that the 4f orbit becomes occupied can be ruled out on the following basis. If this hypothesis is to be accepted, the energy of the 4f state must be close to that of the 6s band in the compressed metal (about $-0.3 Ry$). This can be true only if the effective potential for 4f has an attractive trough² in the neighborhood of $r=0.5 a_H$ (r =distance from nucleus, a_H =Bohr radius for hydrogen), as is the case for the rare earths and for the heavier elements. Integration of the Schroedinger equation shows that the trough must be at least 7 to 8 Ry deep for the existence of a stationary state. The first element for which the 4f function is internal is cerium, $Z=58$. A change of nuclear charge by one unit changes the potential at $r=0.5 a_H$ by about 1 Ry , as is shown by an estimate based on the Thomas-Fermi potential. Hence for cesium, $Z=55$, the potential valley is insufficient by a few Rydberg units to give an internal 4f function. This conclusion remains valid throughout the pressure range studied by Bridgman, because in this range the compression has a negligible effect on the potential near the nucleus.

A shift of the valence electron to 5d is made plausible by spectroscopic evidence. Table I gives the energy of

configurations³ involving d and s states of the K, Rb and Cs atoms and of the corresponding alkaline earth ions. The difference in energy between the d state and the s state decreases with increasing Z and with increasing ionization. In both cases, the potential acting on the valence electron becomes more attractive. In the compression of a metal, the valence electrons are brought closer to the nucleus inside each lattice cell, hence the distance between the 6s band and the 5d band of cesium is expected to decrease with decreasing volume. As is shown by the calculations (see Section II), an overlapping of the two bands occurs at the smaller volumes and affords an explanation of the phase transition.

II. THE ENERGY OF THE 6s AND 5d BANDS

The pressure is given by $-\partial E/\partial V$, where E is the energy and V is the volume per atom of the lattice. In order to obtain E , the positions of the 6s and 5d bands were determined by the method of Wigner and Seitz.⁴ In this method the cellular polyhedron surrounding each nucleus is replaced by a sphere of volume V which will be called the s sphere. The lowest level of a band is obtained by solving the Schroedinger equation inside the s sphere, subject to the condition $\partial\psi/\partial r=0$ at $r=r_0$, where r_0 is the radius of the sphere. Somewhat

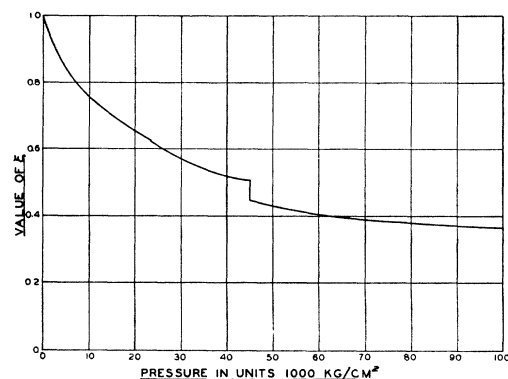


FIG. 1. Volume of cesium as a function of the pressure. The ordinate ξ is the ratio of the volume to the volume at normal pressure. (From Bridgman, reference 1.)

* This paper was written as a Ph.D. thesis in the Department of Physics, University of Chicago, Chicago, Illinois.

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*** Assisted by the ONR and the AEC.

¹ P. W. Bridgman, *Phys. Rev.* **72**, 533 (1947); *Proc. Am. Acad. Arts Sci.* **76**, 55 (1948). I am very much indebted to Professor Bridgman for sending me a table of the volume compression of the alkalis before publication.

² M. G. Mayer, *Phys. Rev.* **60**, 184 (1941).

³ From R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

⁴ E. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933); **46**, 509 (1934).

TABLE I. Energy in Ry units of s and d states for K, Rb, and Cs and the corresponding alkaline earth ions. The zero of energy corresponds to ionization of the valence electron. (From Bacher and Goudsmit, reference 3.)

K	4s	-0.3190	Ca II	4s	-0.8725
	3d	-0.1227		3d	-0.7478
Rb	5s	-0.3070	Sr II	5s	-0.8106
	4d	-0.1306		4d	-0.6764
Cs	6s	-0.2862	Ba II	6s	-0.7350
	5d	-0.1535		5d	-0.6862

different potentials, V_{6s}' and V_{5d}' , were used for 6s and 5d. The determination of these potentials is described in Section III. They are based on the Hartree-Fock equations and are adjusted to give agreement with the respective atomic levels, $E_{6s} = -0.2862$ Ry and $E_{5d} = -0.1535$ Ry. In Table II the energies E_{6s}^B and E_{5d}^B of the bottom of the 6s and of the 5d band are given as a function of r_0 . These energies are also shown in Fig. 2. Below each r_0 , we have listed the corresponding ratio V/V_{th} where V_{th} is the volume at normal pressure obtained from the present calculations. As shown below, V_{th} corresponds to $r_0 = 5.92 a_H$; the experimental value is $5.59 a_H$. We note that in an accurate calculation, the atomic 5d level would split into two levels for zero wave-number, one twofold and one threefold degenerate. This splitting is not obtained in the s sphere approximation. However, it is believed that it would not affect the essential results of the present work.

The width of the bands will now be determined. For each band we let p_0 be the momentum for the highest filled level and E_F the width of the occupied region, on the assumption that all valence electrons occupy levels in the band considered. For the 6s band,

$$p_0 = (9\pi/4)^{1/3} (\hbar/r_0). \quad (1)$$

For the 5d band, there are five zones which correspond in the present method to the values of the magnetic quantum number M . On the assumption that levels having the same wave number vector but different M are degenerate, the density of states is five times the density for the 6s band, and p_0 is smaller than (1) by a factor $5^{1/3}$.

The width E_F would be $p_0^2/(2m)$ if the electrons could be considered as perfectly free. Wigner and Seitz⁵ have treated the effect of the ion cores on the band width by perturbation theory. They found that the energy $E_{\mathbf{k}}$ of the wave with wave number vector \mathbf{k} is given by

$$E_{\mathbf{k}} = E_0 + \frac{\hbar^2 \mathbf{k}^2}{2m} \left[1 - \frac{2\hbar^2}{m\mathbf{k}^2} \sum_{\lambda} \frac{|\int (\mathbf{k} \cdot \text{grad} \psi_0) \psi^{\lambda*} d\mathbf{r}|^2}{E_{\lambda} - E_0} \right], \quad (2)$$

where E_0 and ψ_0 are the energy and the wave function

⁵ See, for example, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book, Company, Inc., New York, 1940), Chapters IX and X.

TABLE II. Position of the bottom of the 6s and of the 5d band for various r_0 . Energies are in Ry units, r_0 is in units a_H .

r_0	$-E_{6s}^B$	$-E_{5d}^B$
6.0	0.4151	
5.8	0.4217	
5.6	0.4267	0.2371
5.4	0.4303	0.2419
5.2	0.4322	0.2473
5.0	0.4308	0.2533
4.8	0.4263	0.2598
4.6	0.4140	0.2673
4.4	0.3948	0.2764
4.2	0.3617	0.2855
4.0	0.3108	0.2972

for the bottom of the band, respectively; the sum extends over all eigenfunctions ψ^{λ} of the Schroedinger equation,

$$-(\hbar^2/2m)\Delta\psi^{\lambda} + V_0\psi^{\lambda} = E^{\lambda}\psi^{\lambda}, \quad (3)$$

which is to be solved inside the s sphere, subject to the condition $\psi^{\lambda} = 0$ at $r = r_0$; E^{λ} is the eigenvalue and V_0 is the potential representing the interaction with the core. In Eq. (2) the integral extends over the s sphere. If E_0 and E^{λ} are expressed in Ry and lengths are in units a_H , one obtains

$$E_F = \frac{p_0^2}{2m} \left[1 - \sum_{\lambda} \frac{4|\alpha_{\lambda}|^2}{E^{\lambda} - E_0} \right], \quad (4)$$

with

$$\alpha_{\lambda} = 2\pi \int_0^{\pi} \int_0^{r_0} (\partial\psi_0/\partial r) \cos\theta \psi^{\lambda*} r^2 dr \sin\theta d\theta. \quad (5)$$

Here θ is the angle between the radius vector in the integrand and the axis of quantization of the spherical harmonics of ψ_0 and ψ^{λ} . For the 6s band the p states⁶ give,

$$\alpha_{\lambda} = (1/\sqrt{3}) \int_0^{r_0} (dR_{6s}/dr) R_{\lambda}^{(p)} r^2 dr, \quad (5a)$$

where R_{6s} is the wave function for the bottom of the 6s band, $R_{\lambda}^{(p)}$ is the radial part of the p function ψ^{λ} ; the normalization is

$$\int_0^{r_0} R_{6s}^2 r^2 dr = \int_0^{r_0} (R_{\lambda}^{(p)})^2 r^2 dr = 1.$$

Table III gives the values of α_{λ} and the corresponding energy denominators for several r_0 . The sign of α_{λ} pertains to the choice in which all functions have the same sign near $r=0$. In calculating the 6p, 7p and 8p functions the potential V_0 in Eq. (4) was taken as V_{6s}' . For 4p the Hartree⁶ function for Cs⁺ was used, and the 5p functions were determined by means of the potential V_{5p} described below. Including a correction for the p states not listed in the table, one obtains the values of the square bracket in Eq. (4) which are tabulated as m/m_{6s}^* ; m_{6s}^* is the effective mass for the 6s band.

⁶ D. R. Hartree, Proc. Roy. Soc. 143, 506 (1934).

As a check on the reliability of Eq. (4), the fourth-order perturbation term was calculated. This term gives the following contribution to the average energy,⁷

$$(3p_0^2/10m)(1.315\lambda_2/r_0^2), \quad (6)$$

where

$$\lambda_2 = \lambda_1 \sum_{\lambda} \frac{8|\alpha_{\lambda}|^2}{(E^{\lambda} - E_0)^2}, \quad (6a)$$

and

$$\lambda_1 = 1 - m/m_{6s}^* = \sum_{\lambda} \frac{4|\alpha_{\lambda}|^2}{E^{\lambda} - E_0}. \quad (6b)$$

The factor $1.315 \lambda_2/r_0^2$ is shown as Δ in Table III. It is seen that the fourth-order correction is small, except in the region of small r_0 . It was not included in the compressibility calculations.

For the $5d$ zone with magnetic quantum number M , $\alpha_{\lambda M}$ is given by

$$\alpha_{\lambda M} = \int_0^{\pi} \int_0^{r_0} (dR_{5d}/dr) \Theta_{2^M} \cos\theta \Theta_{l^M} R_{\lambda} r^2 dr \sin\theta d\theta, \quad (7)$$

where R_{5d} is the radial function for the bottom of the $5d$ band, Θ_{L^M} is the spherical harmonic pertaining to quantum numbers L and M , R_{λ} is the radial part of ψ^{λ} , l is the azimuthal quantum number of ψ^{λ} ; the normalization is

$$\int_0^{r_0} R_{5d}^2 r^2 dr = \int_0^{r_0} R_{\lambda}^2 r^2 dr = 1; \quad \int_0^{\pi} |\Theta_{L^M}|^2 \sin\theta d\theta = 1.$$

$\alpha_{\lambda M}$ vanishes unless $l=1$ or $l=3$; hence only p and f states contribute. Because of the dependence of $\alpha_{\lambda M}$ on M , the degeneracy of the levels for the same wave vector κ is removed. By determining κ for the highest occupied state in each zone, it is found, for

$$|\alpha_{\lambda M}|^2 / (E^{\lambda} - E_0) \ll 1,$$

that E_F is given by Eq. (4), if one takes

$$|\alpha_{\lambda}|^2 = (1/5) \sum_{M=-2}^2 |\alpha_{\lambda M}|^2, \quad (8)$$

and

$$p_0 = (9\pi/20)^{1/2} \hbar / r_0. \quad (1a)$$

We thus obtain

$$\alpha_{\lambda} = \begin{cases} (2/15)^{1/2} \int_0^{r_0} (dR_{5d}/dr) R_{\lambda} r^2 dr, & (l=1) \\ (1/5)^{1/2} \int_0^{r_0} (dR_{5d}/dr) R_{\lambda} r^2 dr. & (l=3). \end{cases} \quad (8a)$$

Table IV gives the values of α_{λ} and the corresponding energy denominators. Including a correction for the p and f states not listed, one obtains the values of the square bracket in Eq. (4) which are tabulated as

⁷ F. Seitz, Phys. Rev. 47, 400 (1935).

m/m_{5d}^* . The contribution of the f states to the sum in Eq. (4) is shown as S_f . The fourth-order perturbation term is negligible for the $5d$ band.

When the appropriate width is added to E_{6s}^B and to E_{5d}^B , one obtains the energy of the highest occupied level on the assumption that all valence electrons are in $6s$ or in $5d$ states, respectively; these energies are given as E_{6s}^T and E_{5d}^T in Fig. 2. This figure shows that at $r_0 = 5.22 a_H$, the curve for the bottom of $5d$ intersects the curve for the top of $6s$. As the metal is further compressed electrons from the top of $6s$ move into $5d$. The fraction g of the electrons which occupies $5d$ can be obtained from the following equation for the energy E^T of the highest occupied level,

$$E^T = E_{6s}^B + (E_{6s}^T - E_{6s}^B)(1-g)^{1/3} \\ = E_{5d}^B + (E_{5d}^T - E_{5d}^B)g^{1/3}. \quad (9)$$

The shift to the $5d$ zones is rapid. The reasons are that E_{5d}^B decreases, while E_{6s}^B increases with decreasing volume and that the $5d$ band has a greater density of levels than the $6s$ band. The different behavior of the $6s$ and $5d$ curves for the lowest states is due to the smaller number of radial nodes of the $5d$ function (see Fig. 3). The minimum of the energy curve arises from the combined effect of the kinetic and the potential energy. The former increases with decreasing volume because of the decreasing effective wave-length of the electrons, while the potential energy is lowered in a compression. The volume at which the first effect predominates is smaller for $5d$ than for $6s$, because of the relative position of the outermost nodes.

The average energy E^A of the valence electrons is obtained by adding the mean translational energy to the energy of the lowest level of each band. We have,

$$E^A = (1-g)[E_{6s}^B + 3/5(E^T - E_{6s}^B)] \\ + g[E_{5d}^B + 3/5(E^T - E_{5d}^B)]. \quad (10)$$

The curve of E^A is shown in Fig. 2. The minimum at $r_0 = 5.86 a_H$ corresponds to normal pressure. With decreasing r_0 , presumably between $4 a_H$ and $5 a_H$, E^A ceases to be a good approximation to the total energy, because of the repulsion of the $5s$ and $5p$ shells. Hence

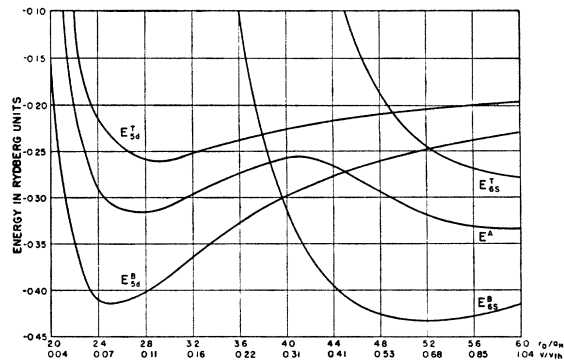


FIG. 2. Position of the $6s$ and $5d$ bands and average energy E^A , as a function of r_0 or of V/V_{4H} .

TABLE III. Values of α_λ and of $E^\lambda - E_0$ for obtaining m/m_{6s}^* and values of m/m_{6s}^* for various radii r_0 . Energies are in Ry units, r_0 is in units a_H .

	r_0	5.8	5.2	4.6	4.0
4p	α_λ	0.214	0.216	0.274	0.466
	$E^\lambda - E_0$	-11.3	-11.3	-11.3	-11.4
5p	α_λ	0.276	0.281	0.357	0.601
	$E^\lambda - E_0$	-0.84	-0.83	-0.83	-0.89
6p	α_λ	-0.011	-0.028	-0.081	-0.199
	$E^\lambda - E_0$	0.79	1.08	1.52	2.211
7p	α_λ	-0.087	-0.095	-0.128	-0.258
	$E^\lambda - E_0$	2.62	3.45	4.70	6.58
8p	α_λ	-0.092	-0.096	-0.138	-0.250
	$E^\lambda - E_0$	5.24	6.74	8.96	12.68
	m/m_{6s}^*	1.349	1.372	1.592	2.555
	Δ	-0.012	-0.017	-0.056	-0.479

the second minimum at $r_0 = 2.79 a_H$ has no direct significance.

In order to obtain some information on the effects due to 5s and 5p electrons, the energies for the bottom and the top of the 5s and 5p bands were calculated by integrating the Schroedinger equation subject to the conditions $\partial\psi/\partial r = 0$ (bottom) and $\psi = 0$ (top⁸) at $r = r_0$. The potentials V_{5s} and V_{5p} used in these integrations are obtained in Section III. Table V gives the energies E_{5s}^B and E_{5s}^T for the bottom and the top of 5s and the energies E_{5p}^B and E_{5p}^T for the bottom and the top of 5p.

The contribution E_{int} of 5s and 5p to the total energy E is given by

$$E_{\text{int}}(r_0) = 2E_{5s}^A(r_0) + 6E_{5p}^A(r_0) - 2E_{5s} - 6E_{5p}. \quad (11)$$

TABLE IV. Values of α_λ and of $E^\lambda - E_0$ for obtaining m/m_{5d}^* and values of S_f and m/m_{5d}^* for various radii r_0 . Energies are in Ry units, r_0 is in units a_H .

	r_0	5.2	4.6	4.0
4p	α_λ	0.159	0.181	0.212
	$E^\lambda - E_0$	-11.5	-11.4	-11.4
5p	α_λ	-0.034	-0.044	-0.060
	$E^\lambda - E_0$	-1.01	-0.98	-0.91
6p	α_λ	-0.044	-0.049	-0.055
	$E^\lambda - E_0$	0.89	1.37	2.19
7p	α_λ	-0.030	-0.033	-0.038
	$E^\lambda - E_0$	3.27	4.55	6.57
8p	α_λ	-0.025	-0.027	-0.028
	$E^\lambda - E_0$	6.56	8.82	12.67
4f	α_λ	0.085	0.106	0.136
	$E^\lambda - E_0$	0.57	0.61	0.67
5f	α_λ	0.079	0.077	0.068
	$E^\lambda - E_0$	1.41	1.80	2.37
6f	α_λ	0.017	-0.004	-0.041
	$E^\lambda - E_0$	3.23	4.10	5.47
	S_f	0.077	0.095	0.128
	m/m_{5d}^*	0.913	0.897	0.865

⁸ J. C. Slater, Phys. Rev. 45, 794 (1934).

Here E_{5s}^A and E_{5p}^A are the average energies of the electrons in the 5s and the 5p band; E_{5s} and E_{5p} are the atomic levels for the potentials V_{5s} and V_{5p} , respectively. A theoretical determination of E_{int} , which would require a calculation of the distribution of levels in the two bands, was not carried out. E_{int} is expected to increase rapidly with decreasing r_0 at the smaller volumes, since it includes the exchange repulsion. This effect will be discussed below. Here we note that the second estimate given in this discussion, which leads to a repulsion energy of 0.024 Ry at $r_0 = 4.0 a_H$, can be correlated with the calculation of the bands, if one assumes that the average energy in each band is related to the energies for the lowest and highest levels by the following equations.

$$\begin{aligned} E_{5s}^A &= \alpha E_{5s}^B + (1-\alpha)E_{5s}^T, \\ E_{5p}^A &= \alpha E_{5p}^B + (1-\alpha)E_{5p}^T, \end{aligned} \quad (12)$$

where α is a constant parameter independent of r_0 . One finds that for $\alpha = 0.39$, $E_{\text{int}}(r_0)$ (see Eq. (11)) agrees with the estimate of the repulsion energy throughout the range of r_0 .

For the energy of interaction between the free electrons we used the following expression, taken from the treatment of Wigner and Seitz,⁵

$$E_f = \frac{0.6e^2}{r_0} - \frac{0.458e^2}{r_0} - \frac{0.288e^2}{r_0 + 5.1 a_H}. \quad (13)$$

The terms in (13) represent, respectively, the Coulomb repulsion, the exchange interaction and the electrostatic correlation.

The cohesive energy and the radius r_0 at normal pressure will now be compared with experiment. The curve of $E^A + E_f$ has a minimum of -0.3374 Ry which lies at $5.92 a_H$. One thus finds a theoretical cohesive energy of 16.1 kg cal./mole. The heat of sublimation⁹ is 18.8 kg cal./mole. Upon making the appropriate temperature correction ($300 \times (6-3) = 900$ cal./mole), one obtains 19.7 kg cal./mole for the experimental cohesive energy. The experimental value of r_0 is $5.59 a_H$. Thus the agreement with experiment is comparable to that obtained in similar calculations⁵ for lithium, sodium and potassium.

Table VI gives the energy E_{th} , defined by

$$E_{th} = E^A + E_f$$

and the increase of energy ΔE_{th} ,

$$\Delta E_{th}(r_0) = E_{th}(r_0) - E_{th}(5.92 a_H).$$

We note that E_{th} and ΔE_{th} do not include the exchange repulsion, which will be discussed below. The experimental increase of energy, to be denoted by ΔE_{exp} , will now be obtained from Bridgman's measurements. In first approximation the increase of internal energy in a compression through dV is PdV (P =pressure).

⁹ F. Seitz, reference 5, p. 3.

The heat released by the sample in this compression is

$$-T(\partial S/\partial V)_T dV = T(\partial P/\partial V)_T (\partial V/\partial T)_P dV,$$

where T is the temperature which will be taken as 0°C , and S is the entropy per atom. In order to evaluate this term, $(\partial P/\partial V)_T$ can be obtained from the observed compression. The dependence of $(\partial V/\partial T)_P$ on the pressure is not known for cesium. $(\partial V/\partial T)_P$ was therefore estimated on the basis of Bridgman's measurements¹⁰ of the expansion coefficient for lithium, sodium and potassium up to $20,000 \text{ kg/cm}^2$. It was found that the heat given up in the compression to $100,000 \text{ kg/cm}^2$ is only 0.002 Ry per atom. We now define,

$$\Delta E_{\text{exp}}(r_0) = \int_{V_{\text{exp}}(r_0/5.92 a_H)^3}^{V_{\text{exp}}} [P - T(\partial S/\partial V)_T] dV, \quad (14)$$

where $V_{\text{exp}} = (4\pi/3)(5.59 a_H)^3$ is the experimental volume per atom at normal pressure and absolute zero. Equation (14) implies that we compare points on the experimental and the theoretical curves of energy *vs.* volume which correspond to equal ratios of the volume to the volume for the minimum of the curve. Because of the thermal expansion, V_{exp} is a fraction $(1+273\beta)^{-3}$ of the volume at normal pressure and 0°C , where β is the linear expansion coefficient; upon taking¹¹ $\beta = 97 \times 10^{-6}$ one finds a value of 0.925. Hence if ξ denotes the observed ratio of volume to volume at normal pressure (see Fig. 1), Eq. (11) becomes

$$\Delta E_{\text{exp}}(r_0) = \frac{V_{\text{exp}}}{0.925} \int_{0.925(r_0/5.92 a_H)^3}^{0.925} [P - T(\partial S/\partial V)_T] d\xi. \quad (14a)$$

ΔE_{exp} is given in Table VI. This table also lists the average pressure $P_a(r_0)$ for the region between r_0 and $r_0 + \delta$ ($\delta =$ interval for which r_0 is tabulated), calculated as follows,

$$P_a(r_0) = \frac{\Delta E_{th}(r_0) - \Delta E_{th}(r_0 + \delta)}{4\pi(r_0 + \frac{1}{2}\delta)^2 \delta}$$

The value which P_a would have if the electrons were restricted to the $6s$ zone is given as P_{6s} . In the last column $P_{\text{exp}}(r_0)$ is the observed pressure, extrapolated

TABLE V. Position of the $5s$ and of the $5p$ band for various r_0 . Energies are in Ry units, r_0 is in units a_H .

r_0	$-E_{5s}^B$	$-E_{5s}^T$	$-E_{5p}^B$	$-E_{5p}^T$
5.8	2.491	2.491	1.271	1.265
5.2	2.492	2.490	1.278	1.261
4.6	2.497	2.487	1.299	1.247
4.0	2.518	2.473	1.357	1.205

¹⁰ P. W. Bridgman, Proc. Am. Acad. **70**, 71 (1934).

¹¹ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926), first edition, Volume I, p. 104.

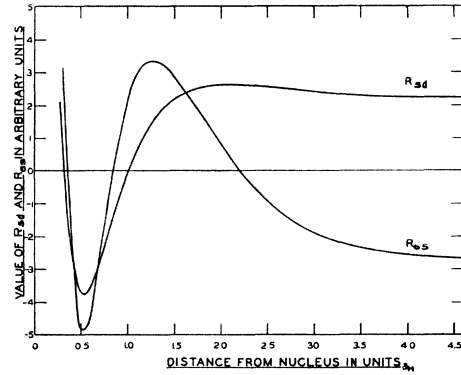


FIG. 3. Wave functions R_{6s} and R_{5d} for the radius $r_0 = 4.6 a_H$ of the s sphere.

to absolute zero, for the volume

$$V_{\text{exp}}[(r_0 + \frac{1}{2}\delta)/5.92 a_H]^3.$$

Since P_a does not include the exchange repulsion, it cannot be compared directly with P_{exp} at the smaller volumes. However $P_{6s} - P_a$ depends only on the position of the bands and shows the effect of the $5d$ states.

The volume discontinuity and the exchange repulsion will now be discussed. The observed limits of the discontinuity correspond to

$$\begin{aligned} V/V_{\text{exp}} &= 0.506/0.925 = 0.547, \\ V/V_{\text{exp}} &= 0.449/0.925 = 0.485. \end{aligned}$$

Here 0.506 and 0.449 are the values of ξ at the limits of the transition; the factor $1/0.925$ takes into account the thermal expansion at normal pressure. For the existence of a volume discontinuity it is necessary that the curve of total energy E *vs.* V have a region of downward curvature; the volume changes discontinuously between the two points with common tangent. Figure 4 shows the energies ΔE_{exp} and ΔE_{th} . The curve of ΔE_{th} is approximately a straight line in the region from $V/V_{th} = 0.55$ to 0.4 . In order to obtain the curvature of E , the ionic repulsion energy must be added to ΔE_{th} . For an estimate of the repulsion term we use the expression due to Born and Mayer¹² for the interaction between two neighboring ions, to be denoted

TABLE VI. Energy terms and values of the pressure. Energies are in Ry units, pressures are in units 1000 kg/cm^2 , r_0 is in units a_H .

r_0	$-E_{th}$	ΔE_{th}	ΔE_{exp}	P_a	P_{exp}	P_{6s}
5.8	0.3369	0.05×10^{-2}	0.05×10^{-2}			
5.6	0.3342	0.32	0.28	5.0	4.9	
5.4	0.3292	0.82	0.73	9.9	11	
5.2	0.3213	1.61	1.48	17	19	
5.0	0.3073	3.01	2.48	32	27	38
4.8	0.2920	4.54	3.74	38	39	55
4.6	0.2757	6.17	5.20	44	45	95
4.4	0.2604	7.70	6.96	45	60	182

¹² M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

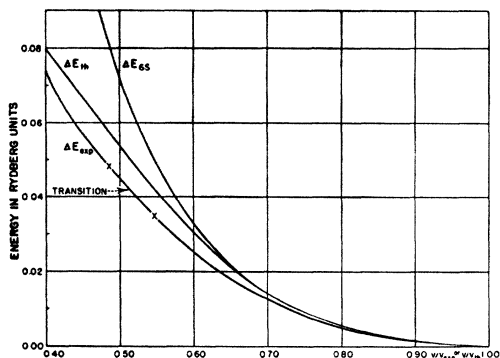


FIG. 4. Increase of energy ΔE_{exp} as a function of V/V_{exp} ; the theoretical results ΔE_{th} and ΔE_{6s} are plotted versus V/V_{th} . The repulsion energy must be added to ΔE_{th} in order to obtain the theoretical total energy.

by E_{ion} ,

$$E_{\text{ion}} = A \exp[(2r_i - D)/a]. \quad (15)$$

Here D is the distance between the nuclei, r_i is the ionic radius, A and a are constants whose values will be taken first from the work of Bardeen¹³ $A = 1.25 \times 10^{-12}$ erg, $r_i = 1.75A$, $a = 0.21A$. It will be assumed that the lattice is close-packed, in accordance with Bardeen's explanation¹³ of the transition at 23,000 kg/cm² as due to the change from the body-centered to a close-packed structure. One finds that the repulsion energy per atom, $6E_{\text{ion}}$, increases from 0.0047 Ry at $r_0 = 4.6 a_H$ to 0.072 Ry at $r_0 = 4.0 a_H$. The increase of E_{ion} is sensitive to the constants in the exponent. The constants obtained by Huggins and Mayer,¹⁴ $r_i = 1.455A$, $a = 0.345A$, $A = 1.25 \times 10^{-12}$ erg, would lead to an increase of $6E_{\text{ion}}$ from 0.0046 Ry at $r_0 = 4.6 a_H$ to 0.024 Ry at $r_0 = 4.0 a_H$. These estimates are compatible with the assumption that the repulsion energy does not become important until the metal is compressed to about $r_0 = 4.5 a_H$ ($V/V_{th} = 0.44$). On this basis there is a region between $V/V_{th} \sim 0.55$ and $V/V_{th} \sim 0.44$ in which the curve of E , as obtained here, is approximately a straight line. This result may be taken as an indication of the observed phase transition. It should be emphasized that an exact agreement with the details of the compressibility curve cannot be expected, on account of the approximations made in the calculation of the energy.

According to the present picture, the repulsion energy effectively determines the lower limit of the transition, which otherwise would extend to a smaller volume, as is shown by the curve of E^4 in Fig. 2. A comparison with the increase of ΔE_{exp} indicates that the repulsion energy probably is sufficiently large to account for the low compressibility above the transition. We note that when the repulsion energy is added to ΔE_{th} for $V/V_{th} = 0.40$, the resulting increase of the total energy is between 1.2 and 1.5 times the observed value ΔE_{exp} .

¹³ J. Bardeen, J. Chem. Phys. 6, 372 (1938).

¹⁴ M. L. Huggins and J. E. Mayer, J. Chem. Phys. 1, 643 (1933).

It is believed that this disagreement lies within the uncertainty of the calculations.

In Fig. 4 we have also shown the increase of energy ΔE_{6s} , obtained by assuming that all valence electrons are in 6s,

$$\Delta E_{6s}(r_0) = E_{6s}^A(r_0) + E_f(r_0) - E_{th}(5.92 a_H),$$

where E_{6s}^A is the average energy for the states of the 6s band. ΔE_{th} is in much closer agreement with the experimental curve than ΔE_{6s} . The repulsion energy, which must be added to ΔE_{6s} , would further increase the departure of the 6s curve from the experimental results.

It is of interest to examine the behavior of E near the volume at which 5d begins to overlap the occupied region of 6s; this volume will be denoted by V_1 . It will be shown that the term in E , associated with the occupation of 5d, varies as $(V_1 - V)^{5/2}$. In first approximation, $E_{6s}^T - E_{5d}^B$ is linear in $V_1 - V$, so that the number of 5d electrons is proportional to $(V_1 - V)^{3/2}$. Since the energy of these electrons is lowered by an amount of the order of $E_{6s}^T - E_{5d}^B$, one finds a dependence $(V_1 - V)^{5/2}$ for the change of the average energy. If the term in E is written as $-\eta(V_1 - V)^{5/2}$ ($\eta > 0$), we have

$$\left(\frac{d^2 E}{dV^2} = \frac{d^2 E}{dV^2} \right)_{V_1} = \frac{15}{4} \eta (V_1 - V)^{3/2} + \dots, \quad (V < V_1) \quad (16)$$

for small $V_1 - V$. The term $d^2 E/dV^2$ at V_1 is characteristic of 6s and is positive. Because of the second and higher terms in the expansion, $d^2 E/dV^2$ becomes negative unless the exchange repulsion predominates. The limits of the discontinuity lie outside the region where $d^2 E/dV^2 < 0$ and the upper limit is not expected to coincide with V_1 . Thus for small η or strong ionic repulsion, the transition tends to occur after the bands have begun to overlap. We note that the 6s-5d overlapping occurs for $V_1/V_{th} = 0.686$, while the transition starts at $V/V_{\text{exp}} = 0.547$.

If the present explanation is correct, the phase transition is associated with a marked increase of the magnetic susceptibility. For perfectly free electrons, the susceptibility (per gram) χ_p due to spin paramagnetism¹⁵ is

$$\chi_p = \frac{3N_0}{2AE_F} \left(\frac{e\hbar}{2mc} \right)^2, \quad (17)$$

($N_0 = \text{Avogadro's number}$, $A = \text{atomic weight}$). Upon taking $E_F = p_0^2/(2m^*)$ (see Eq. (4)), we find $\chi_p = 0.090 \times 10^{-6}$ for the 6s band and 0.448×10^{-6} for the 5d band, at $r_0 = 4.40 a_H$ (lower limit of transition). For the total susceptibility χ we obtain

$$\chi = \frac{2}{3}(0.45 \times 10^{-6}) - 0.29 \times 10^{-6} = 0.01 \times 10^{-6}.$$

Here the factor $\frac{2}{3}$ accounts for the diamagnetism of the

¹⁵ See, for example, F. Seitz, reference 5, p. 160.

free electrons and the second term is the contribution of the ion core.¹⁶ A similar estimate for normal pressure¹⁷ gives $\chi = -0.13 \times 10^{-6}$.

The absence of similar transitions for potassium and rubidium¹ in the range up to 100,000 kg/cm² will now be discussed. The separation of the atomic d and s levels (Table I) suggests that a greater increase of energy than for cesium is required to raise the s band above the lowest d level. The work done in the compression to 100,000 kg/cm², as obtained from Bridgman's data,¹ is 0.044 Ry for potassium and 0.059 Ry for rubidium. While these values exceed the work for cesium up to 45,000 kg/cm² (0.037 Ry), the increase of energy may be insufficient to produce the transition.

This possible explanation will be considered in greater detail. At 100,000 kg/cm² the energy E per atom is

$$E = -E_i - E_c + W, \quad (18)$$

where E_i is the ionization potential, E_c and W denote, respectively, the cohesive energy at normal pressure and the work done in the compression, both extrapolated to absolute zero. With E_i as given in Table I and E_c obtained from the heat of sublimation,⁹ one finds $E = -0.343$ Ry for potassium and -0.313 Ry for rubidium at 100,000 kg/cm², while the energy for cesium is -0.312 Ry at the start of the transition (45,000 kg/cm²). In view of the results obtained for cesium, it seems reasonable to expect that the start of the transition will lie close to the volume at which the average energy of the states of the s band equals the energy of the lowest d level. On the assumption that the ionic repulsion is small and that most valence electrons occupy s levels at the pressure for which E has been calculated, E gives approximately the average energy of the s band. On this basis a comparison of the values of E shows that a phase transition below 100,000 kg/cm² is unlikely for potassium and rubidium, if the bottom of the d band at 100,000 kg/cm² lies at a higher energy than the bottom of $5d$ for cesium at the start of the transition. From the observed compression, one obtains $r_0 = 3.92 a_H$ for potassium and $r_0 = 4.14 a_H$ for rubidium at 100,000 kg/cm², while the radius for cesium at 45,000 kg/cm² is $4.57 a_H$. The energy of d levels is lowered in a compression; the fact that r_0 is smaller for potassium and rubidium tends to favor a lower energy than for cesium. On the other hand, the relative position of the d levels of the three alkalis for a given r_0 is not known. If the trend is the same as for the atomic levels, the energy increases in the order of decreasing Z . This effect would tend to compensate the effect of the smaller radius. A definite conclusion cannot be drawn from these considerations. If the present explanation is correct, a volume discontinuity should occur above 100,000 kg/cm², in the region in which the shift of the

electrons from the s to the d states is most rapid, unless the ionic repulsion predominates at the corresponding volume.

III. THE EFFECTIVE POTENTIALS

In this section the calculations leading to the potentials V_{6s}' and V_{5d}' will be described. The main part of this work was concerned with the determination of the potential energy terms in the Hartree-Fock equations for the $6s$ and $5d$ wave functions.

The calculations were based on Hartree's field without exchange⁶ for Cs⁺. The wave functions for $1s$, $2s$, \dots , $4d$ were taken from Hartree's work and the Hartree-Fock equations were solved to a sufficient approximation for $5s^2 5p^6 6s$ with boundary conditions appropriate to the metal for $r_0 = 4.6 a_H$. In this calculation it was assumed that all free electrons occupy $6s$ states. For $5s$ and $5p$ two functions were considered at each stage of the calculation, namely, those for the lowest and the highest state of the band, satisfying the conditions $\partial\psi/\partial r = 0$ and $\psi = 0$ at $r = r_0$, respectively. It was assumed that the electrostatic potential due to $5s$ and $5p$ for the next stage of the calculation is the same as if half the electrons of each zone occupied the lowest and half the highest state. For $6s$ the effective charge distribution was obtained from a single wave function determined from the boundary condition,

$$(\partial\psi/\partial r) + 1/2(\psi/r) = 0$$

at $r = r_0$, which is intermediate between the boundary conditions for the lowest and the highest state of the zone. The preceding approximations do not significantly affect the potentials for $6s$ and $5d$, because the difference between the wave functions for the lowest and the highest occupied state of each zone is small for $r_0 = 4.6 a_H$.

The potential due to the $1s$, $2s$, \dots , $4d$ electrons was obtained from Hartree's charge distribution.⁶ The exchange of $5s$, $5p$ and $6s$ with these electrons was represented by an added term in the potential,¹⁸ obtained as follows. Consider two free electrons with wave functions $(1/\sqrt{\Omega}) \exp(i\kappa_1 \cdot \mathbf{r}_1)$, $(1/\sqrt{\Omega}) \exp(i\kappa_2 \cdot \mathbf{r}_2)$; here κ_1 and κ_2 are the wave-number vectors, \mathbf{r}_1 and \mathbf{r}_2 are the position vectors of the electrons, Ω is the volume of normalization. In the Hartree-Fock equation exchange appears as a term¹⁹

$$\left[-\frac{e^2}{\Omega} \int_{\Omega} \frac{\exp(-i(\kappa_1 - \kappa_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2))}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \frac{\exp(i\kappa_1 \cdot \mathbf{r}_1)}{\sqrt{\Omega}} \quad (19)$$

in the equation for electron 1. In the limit $\Omega \rightarrow \infty$ the integral is independent of \mathbf{r}_1 and its value, denoted by K , is

$$K = 4\pi/|\kappa_1 - \kappa_2|^2. \quad (19a)$$

Hence (19) is just a constant times the wave function.

¹⁶ A. Sommerfeld and H. Bethe, *Handbuch der Physik* XXIV/2 (Julius Springer, Berlin, 1933), p. 473.

¹⁷ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936).

¹⁸ I am very much indebted to Dr. J. Steinberger and Professor E. Teller who developed this treatment of exchange.

¹⁹ See, for example, F. Seitz, reference 5, p. 339.

This well-known result for free electrons suggests the following representation of exchange of an outer electron ($5s$, $5p$, $6s$) with one of the inner shells at r . The electrons are considered as free with wave numbers corresponding to their classical kinetic energy. Thus we have,

$$\hbar^2\kappa_i^2/(2m) = \epsilon_i - V_i(r), \quad (i=1, 2)$$

where κ_1 and κ_2 are the wave-numbers, ϵ_1 and ϵ_2 are the Hartree eigenvalues, V_1 and V_2 are the Hartree self-consistent potentials for the outer and the inner shell, respectively. It is assumed that the motion of the inner electrons is isotropic and K is averaged over all orientations of κ_2 . $1/\Omega$ is replaced by the density $(2l_2+1)\psi_2^2(r)$ or the electrons of parallel spin, ψ_2 being the normalized radial Hartree function for the inner shell and l_2 its azimuthal quantum number. The resulting value of the bracket in (19), to be denoted by V_{ex} , is

$$V_{ex} = -\frac{2\pi(2l_2+1)e^2\psi_2^2}{\kappa_1\kappa_2} \log \left| \frac{\kappa_1 + \kappa_2}{\kappa_1 - \kappa_2} \right|. \quad (20)$$

In the equations for $5s$, $5p$ and $6s$, one term V_{ex} was introduced for each inner shell. When V_{ex} , ϵ_i and V_i are in Ry units and ψ_2 is normalized according to

$$\int_0^\infty \psi_2^2 r^2 dr = 1,$$

with r in units a_H , Eq. (20) becomes

$$V_{ex} = -\frac{(2l_2+1)\psi_2^2}{(\epsilon_1 - V_1)^{\frac{1}{2}}(\epsilon_2 - V_2)^{\frac{1}{2}}} \log \left| \frac{(\epsilon_1 - V_1)^{\frac{1}{2}} + (\epsilon_2 - V_2)^{\frac{1}{2}}}{(\epsilon_1 - V_1)^{\frac{1}{2}} - (\epsilon_2 - V_2)^{\frac{1}{2}}} \right|. \quad (20a)$$

In the region where $\epsilon_2 - V_2 < 0$, the limit of (20a) for $\epsilon_2 - V_2 \rightarrow 0$ was taken, giving

$$V_{ex} = -\frac{2(2l_2+1)\psi_2^2}{\epsilon_1 - V_1}. \quad (20b)$$

The potential for exchange based on Eq. (20) will be

TABLE VII. Values of $rV_{6s}' \cdot V_{6s}'$ is in Ry units, r is in units a_H .

r	rV_{6s}'	r	rV_{6s}'
0.00	110	0.8	17.47
0.01	104.41	0.9	14.19
0.02	99.83	1.0	12.45
0.03	95.32	1.2	9.79
0.04	90.68	1.4	8.03
0.06	84.08	1.6	6.70
0.08	78.49	1.8	5.78
0.10	73.91	2.0	5.35
0.15	61.65	2.4	3.13
0.20	53.05	2.8	2.95
0.25	47.02	3.2	2.69
0.30	42.26	3.6	2.51
0.35	37.47	4.0	2.41
0.4	32.61	5.0	2.25
0.5	27.30	6.0	2.15
0.6	23.05	7.0	2.10
0.7	19.58	8.0	2.05

compared below with one obtained directly from the Hartree-Fock equation.

In obtaining the exchange between $5s$, $5p$ and $6s$ the following approximation was made. Let R^B and R^T be the normalized radial functions for the lowest and the highest state, respectively, of $5s$ or $5p$. At any stage when R^B and R^T were obtained, $R^B + R^T$ was normalized and the resulting function, to be denoted by R^A , was used in evaluating the exchange terms involving this band. The expressions for the exchange terms were taken from the tables of Hartree and Hartree²⁰ for closed shells, except for the exchange of $6s$ in the equations for the $5s$ and $5p$ functions. For these terms half the tabulated value was taken, since there is a probability $\frac{1}{2}$ that the $6s$ in the atomic sphere has a given spin direction. We thus obtain the following equation for $5s$, in which u_{5s} is r times the $5s$ function,

$$\begin{aligned} & -\frac{d^2 u_{5s}}{dr^2} + (V_c + V_{ex, 5s} + \mathcal{U}_{5s} + 6\mathcal{U}_{5p} + \mathcal{U}_{6s})u_{5s} \\ & = \epsilon_{5s}u_{5s} + \left[\left(\frac{2}{r^2} \int_0^r u_{5s}^A u_{5p}^A r' dr' \right. \right. \\ & \quad \left. \left. + 2r \int_r^{r_0} u_{5s}^A u_{5p}^A \frac{1}{r'^2} dr' \right) u_{5p}^A \right. \\ & \quad \left. + \left(\frac{1}{r} \int_0^r u_{5s}^A u_{6s} dr' + \int_r^{r_0} u_{5s}^A u_{6s} \frac{1}{r'} dr' \right) u_{6s} \right]. \quad (21) \end{aligned}$$

Here u_{5s}^A and u_{5p}^A are r times the functions R^A for $5s$ and $5p$, respectively; u_{6s} is r times the $6s$ function,²¹ V_c is the potential due to the nucleus and the inner electrons; $V_{ex, 5s}$ is the potential for exchange with $1s$, $2s$, \dots , $4d$; \mathcal{U}_{5s} , \mathcal{U}_{5p} , \mathcal{U}_{6s} are the potentials due to $5s$, $5p$, $6s$, respectively, ϵ_{5s} is the eigenvalue. The potentials and ϵ_{5s} are in Ry units, lengths are in units a_H and the normalization is

$$\int_0^{r_0} (u_{5s}^A)^2 dr = \int_0^{r_0} (u_{5p}^A)^2 dr = \int_0^{r_0} u_{6s}^2 dr = 1.$$

At each stage of the calculation an equivalent potential V_{5s} was obtained by adding to the Coulomb terms on the left side of (21), $-1/u_{5s}^A$ times the exchange terms in the square bracket. The Schroedinger equation with V_{5s} was solved, instead of the inhomogeneous Eq. (21). The same procedure was used for $5p$ and $6s$, involving potentials denoted by V_{5p} and V_{6s} . After a reasonable V_{6s} was obtained, the $6s$ function was kept fixed, while the $5s$ and $5p$ functions were made more self-consistent. The final V_{5s} and V_{5p} of this calculation are the potentials mentioned in Section II. The $6s$ function was then redetermined. It is estimated that

²⁰ D. R. Hartree and W. Hartree, Proc. Roy. Soc. **156**, 45 (1936).

²¹ The terms involving Lagrangian parameters were omitted. However, u_{5s}^A and u_{6s} were nearly orthogonal in the final stages of the calculation; the integral over $u_{5s}^A u_{6s}$ had values ~ 0.03 .

the resulting V_{6s} differs by less than 0.04 Ry at $r=1.0 a_H$ and 0.01 Ry at $r=4.6 a_H$ from that of a completely self-consistent calculation. Since this uncertainty is smaller than the correction applied to V_{6s} (see below), the approximation to self-consistency was sufficient.

The exchange part of V_{6s} was then improved by replacing the potential for exchange with $1s, 2s, \dots, 4d$ (Eq. (20)) by $1/u_{6s}$ times the corresponding terms²⁰ in the Hartree-Fock equation for $6s$. In evaluating the exchange integrals, Hartree's $1s, 2s, \dots, 4d$ functions⁶ were used. For comparison we shall list some values (in Ry units) of the two exchange potentials; the Hartree-Fock exchange is given in parentheses: 22.7 (25.3) at $r=0.08 a_H$; 3.06 (1.15) at $r=0.4 a_H$; 3.15 (1.65) at $r=0.8 a_H$; 0.884 (0.500) at $r=1.2 a_H$; 0.175 (0.181) at $r=1.6 a_H$. The values given by Eq. (20) are considerably too large between $r=0.4 a_H$ and $1.2 a_H$. We note that for the exchange of $5d$ with $1s, 2s, \dots, 4d$, Eq. (20) gives a better approximation to the Hartree-Fock values; the agreement is within 20 percent for $r < 0.8 a_H$.

The atomic eigenvalue for the resulting potential V_{6s} lies 0.03 Ry above the observed level. It is reasonable to attribute a major part of the discrepancy to the electrostatic correlation of $6s$ with the core electrons.

A small term of the proper magnitude to give agreement with the atomic level was added to V_{6s} . The dependence on r of this term was obtained from a classical model of the correlation. The potential V_{6s}' thus determined is given in Table VII.²²

In determining V_{5d}' the Coulomb interaction with the core was taken from V_{6s} . The exchange contribution was obtained by evaluating the corresponding terms²⁰ in the Hartree-Fock equation for $5d$. As for $6s$, a small attractive term was added to the resulting potential, in order to obtain agreement with the observed atomic level.

IV. ACKNOWLEDGMENTS

I would like to thank Professor E. Fermi, who suggested the line of approach to this problem, and Professor E. Teller for many invaluable discussions. Sincere thanks are also due Professor G. Breit, Professor J. E. Mayer, Dr. J. Steinberger, Professor E. Wigner and Dr. C. N. Yang for very helpful discussions.

²² The rapid decrease of $V_{6s}'r$ between $r=2.0 a_H$ and $r=2.4 a_H$ is not significant. The exchange potential changes from a large positive to a large negative value, because the $6s$ function has a node near $2.2 a_H$. However, the contribution of this term to $V_{6s}'u_{6s}^2$ remains small.

The Magnetic Deviation of Cosmic-Ray Particles in the Atmosphere*

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(Received January 23, 1950)

The paper concerns the possibility of the path of a cosmic-ray α -particle, proton, or mesotron being bent in the atmosphere by the earth's magnetic field in such a manner as to pass vertically upward through a counter telescope.

In order to pass vertically upward through the telescope, it is necessary for the ray to have been horizontal at some time during its path; and taking into account the minimum energies necessitated by absorption along the path, it appears that, for a telescope at an altitude comparable with 100,000 ft., neither an α -particle nor a proton would have "vertical room" between the telescope and the earth to describe the angle ($\pi/2$) necessary to take it from the horizontal to the vertical upward direction. For a mesotron there would be room, but in this case the mesotron "mean life" operates to prevent the phenomenon happening in appreciable degree; it is shown that regardless of energy or the law of energy loss, only a fraction $e^{-11.6}$ of any assigned number of mesotrons can live long enough to travel through a right angle in the earth's magnetic field.

I. INTRODUCTION

THE importance of high altitude measurements with Geiger counter telescopes has occasionally raised the question as to whether such measurements may be influenced by effects of the earth's magnetic field in bending the orbits of protons, α -particles, or mesotrons to the extent of causing rays to enter the telescopes from the under side. It has been thought well to investigate this matter for the case of a vertically directed telescope, the illustration in mind being the

recent observations of Pomerantz.¹ The calculations for an inclined telescope may be carried out in an analogous manner.

II. THE CASE OF PROTONS AND ALPHA-PARTICLES

It is easy to show that for a fixed magnetic field H , the situation is most favorable for resulting in upward rays through the telescope when H is horizontal. We shall consequently confine attention to this case.

* Assisted by the joint program of the ONR and AEC.

¹ M. A. Pomerantz and M. S. Vallarta, *Phys. Rev.* **76**, 1889 (1949); also M. A. Pomerantz, *Phys. Rev.* **77**, 830 (1950).