

General form of  $U$  satisfying these equations simultaneously is

$$U(X_\mu, r_\mu) = \int \cdots \int (d\bar{k})^4 (dI)^4 \delta(k_\mu k^\mu + \kappa^2) \delta(k_\mu l^\mu) \delta(l_\mu l^\mu - \lambda^2) \times b(k_\mu) \exp(i k_\mu X^\mu) \delta(r_1 + l_1) \delta(r_2 + l_2) \delta(r_3 + l_3) \delta(r_4 + l_4). \quad (6)$$

$\delta$ -functions in (6) are equivalent to restrict two four-dimensional integrations with respect to two vectors  $k_\mu$  and  $l^\mu$  to domains satisfying the conditions

$$k_\mu k^\mu + \kappa^2 = 0, \quad l_\mu l^\mu - \lambda^2 = 0, \quad k_\mu l^\mu = 0. \quad (7)$$

A simple physical interpretation can be given to these restrictions. Suppose that the particle is at rest represented by the plane wave vector  $k_1 = k_2 = k_3 = 0$ ,  $k_4 = \pm \kappa$ . In this particular case, the conditions (7) reduce to

$$l_1^2 + l_2^2 + l_3^2 = \lambda^2, \quad l_4 = 0, \quad (8)$$

which mean that the contribution of the particle at rest to the matrix elements of  $U$  is restricted to values of  $r_\mu$  satisfying

$$r_1^2 + r_2^2 + r_3^2 = \lambda^2, \quad r_4 = 0. \quad (9)$$

The operator  $U$  has a character of the wave amplitude rather than the density itself. However, the density operator, which is quadratic or bilinear in  $U$ , has again the matrix elements, which are different from zero only for

$$(r_{12})^2 + (r_{23})^2 + (r_{31})^2 \leq \lambda^2. \quad (10)$$

Since the above formulation is perfectly relativistic, the whole field  $U$  can be regarded as a field theoretical representation of an assembly of elementary particles with the mass  $m$  and the radius  $\lambda$ , which move without any change in their form except the Lorentz contraction associated with the change of the proper time axis. Of course,  $b(k_\mu)$  should be quantized in the usual way in order to make the correspondence with the particle picture complete.

The above arguments can be extended to the vector field with no essential alteration. The case of the Dirac particle is more interesting. We start from the relations

$$\gamma_\mu' [x^\mu, \psi] + \lambda \psi = 0, \quad (11)$$

$$\gamma_\mu' [p_\mu, \psi] + m c \psi = 0, \quad (12)$$

instead of (2) and (3), where  $\psi$  denotes a non-localizable spinor field with four components.  $\gamma^\mu$  are well known Dirac matrices

$$\gamma^1 = i\rho_2\sigma_x, \quad \gamma^2 = i\rho_2\sigma_y, \quad \gamma^3 = i\rho_2\sigma_z, \quad \gamma^4 = \rho_3, \quad (13)$$

forming a four-vector and  $\gamma_\mu'$  are also four Dirac matrices

$$\gamma_1' = \rho_3\sigma_x, \quad \gamma_2' = \rho_3\sigma_y, \quad \gamma_3' = \rho_3\sigma_z, \quad \gamma_4' = -i\rho_2, \quad (14)$$

forming a pseudovector.<sup>6</sup> If we again represent  $\psi$  by four functions of  $X_\mu$  and  $r_\mu$ , we can deduce from (11) and (12) by taking account of the well-known commutation relations between Dirac matrices the result that each of four functions must have the form similar to  $U(X_\mu, r_\mu)$  in (6).

Whether a consistent field theory can be constructed by starting from the above model is, of course, an open question, because the introduction of any kind of extended source is almost inevitably accompanied by the departure from the Schrödinger equation. Probably a formalism, which is more or less similar to Heisenberg's  $S$ -matrix scheme,<sup>7</sup> will be needed for further developments.

Detailed accounts will be made in later issues of this journal and Progress of Theoretical Physics.

The author wants to express his hearty thanks to Professor Oppenheimer for giving him the opportunity of staying at the Institute for Advanced Study, Princeton, and also to Professor Oppenheimer, Professor Uhlenbeck, and Dr. Pais for stimulating discussions.

\* On leave of absence from Kyoto University, Kyoto, Japan.

<sup>1</sup> H. Yukawa, Prog. Theor. Phys. 2, 209 (1947); 3, 205, 452 (1948).

<sup>2</sup> M. Born, Proc. Roy. Soc. A165, 291 (1938); A166, 552 (1938). The idea of reciprocity has been developed since then by Born, Landé, and others in various ways. Very recently, attempts at the problem of masses of ele-

mentary particles were made by M. Born, Nature 163, 207 (1949); H. Green, Nature 163, 208 (1949).

<sup>3</sup> Non-localizable fields were first considered by Markow, J. Phys. 2, 453 (1940). More general considerations were made by Born and Peng, Proc. Roy. Soc. Edinburgh 62, 40, 92, 127 (1944).

<sup>4</sup> The author is indebted to Dr. Pais for informing him of unpublished results.

<sup>5</sup> From the relations (1) and (4), it follows immediately that

$$[x^\mu [p_\mu, U]] = 0.$$

<sup>6</sup>  $\lambda$  is not a pure scalar, but a pseudoscalar, which changes sign by reflection. However, the form of  $\psi$  is not altered by the change of sign of  $\lambda$ .

<sup>7</sup> W. Heisenberg, Zeits. f. Physik 120, 513, 673 (1943); 123, 93 (1944).

## Concerning the High Pressure Allotropic Modification of Cerium\*

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June 1, 1949

CERMIUM has long been recognized<sup>1,2</sup> to exist in two variant crystal forms at normal room temperatures and pressures. One structure is face-centered cubic with  $a=5.14\text{\AA}$ ; the other is close-packed hexagonal with  $a=3.65\text{\AA}$  and  $c=5.91\text{\AA}$ . In addition, Bridgman<sup>3,4</sup> has reported a high pressure transformation at 12,430 atmospheres which appears to be impurity sensitive, and Trombe and Foex<sup>5</sup> have found dilatometric evidence of a low temperature transformation under certain conditions. Bridgman's<sup>4</sup> latest results on presumably pure cerium indicate an over-all contraction in volume of 16.55 percent at 15,000 atmospheres. Trombe and Foex<sup>5</sup> report a contraction of the order of 10 percent at low temperatures which appears to be associated with an anomaly in the paramagnetic susceptibility.<sup>6</sup> It appears highly probable that both the new phases reported are the same.

Attempts were made to resolve the structure of the low temperature modification from x-ray powder diffraction pictures made at 80°K on pure cerium possessing a face-centered structure at room temperature. This cerium was estimated spectroscopically to contain the following impurities:<sup>7</sup> 0.05 percent Mg, 0.03 percent Si, 0.02 percent Fe, 0.001 percent Cu, 0.001 percent Ag. The instrument used which has a dispersion of 5\AA/mm was unable to reveal the presence of other rare earths. Unfortunately, we were unable to induce a low temperature transformation in material of this purity. However, no attempt was made to cold-work the metal when it was cold.

Efforts were consequently devoted to obtaining diffraction pictures of the high pressure modification using the beryllium bomb technique developed by Riley and Lawson.<sup>8</sup> Powder patterns, taken at approximately 15,000 atmospheres, reveal as indicated by Table I, that the high pressure modification of the initially face-centered lattice stable at atmosphere pressure is also face-centered cubic! The new structure possesses a lattice constant  $a=4.84\pm 0.03\text{\AA}$ , yielding an over-all volume change at this pressure of 16.5 percent in good agreement with Bridgman. The uncertainty in the result arises largely from the large diameter of the sample ( $\frac{1}{32}$  in.) demanded by the mechanical design require-

TABLE I. Lattice spacings in face-centered cubic cerium\* at 15,000 atmospheres.

$hkl$	$2r$	$2r - \delta$	$d \times 10^8$	$a \times 10^8$
111	2.02 ± 0.03 cm	1.96 cm	2.75 ± 0.05 cm	4.76 ± 0.09 cm
200	2.30 ± 0.01	2.24	2.42 ± 0.01	4.84 ± 0.02
220	3.23 ± 0.01	3.17	1.71 ± 0.005	4.84 ± 0.02
311	3.78 ± 0.02	3.72	1.46 ± 0.01	4.85 ± 0.03
420	5.14 ± 0.02	5.08	1.077 ± 0.003	4.82 ± 0.02
Average lattice constant $a = 4.84 \pm 0.03$				

\* These spacings were obtained using Mo  $K\alpha$  radiation with a camera whose diameter equals 7.57 cm.  $hkl$  are the Miller indices of the reflecting plane,  $r$  the radius of the diffraction ring,  $\delta$  the correction (equal to 0.06 cm) for the thickness of the specimen as determined from similar patterns obtained at atmospheric pressure,  $d$  the calculated spacing, and  $a$  the calculated lattice constant.

ments of the bomb. Evidence of other lines is present but confused by near coincidence with lines arising from the beryllium. For this reason, they are not included in Table I.

As a result of stimulating conversations with our colleague, W. H. Zachariasen, we propose the following simple model to explain this rather unusual transformation. Cerium, which is the first atom in the periodic table to permit the existence of a 4f electron in the free gaseous state, when condensed exhibits the tendency to become perverted from a trivalent to a quadrivalent state. For instance, CeO<sub>2</sub> is the stable oxide. Apparently, the application of 12,000 atmospheres of pressure is sufficient to evoke this transformation and the 4f electron is literally squeezed into a 5d state. No other model appears capable of explaining the enormous contraction from one closely packed structure to an identical closely packed structure. Quantitatively, this model appears to be supported by the lattice constants observed. Thus, according to W. H. Zachariasen,<sup>9</sup> the ionic radii of trivalent and quadrivalent cerium with a coordination number of 12 should be 1.85±0.01Å and 1.71±0.02Å, respectively; the lattice constants observed correspond to ionic radii of 1.82Å and 1.71±0.02Å to which a small correction of about 1.5 percent should be applied for normal compressibility by comparison with the data on lanthanum and praseodymium. If we assume that the phase observed by Trombe and Foex<sup>5</sup> is also a collapsed face-centered structure, the Clapyron equation permits us to make a rough estimate of the energy level separation between the 4f and 5d states. Such an estimate yields a value of approximately 0.04 ev. In addition, such a change in the electronic configuration of cerium would explain qualitatively the slight decrease in the change of the paramagnetic susceptibility with temperature.<sup>10</sup> Quantitative agreement is not to be expected since the low temperature transformation probably does not go to completion.

The hypothesis proposed above also explains why the transformation, unique to cerium, is absent in lanthanum and praseodymium. In the former, the 5d state is known to be the more stable, while in the latter, the 4f state is probably sufficiently stable to resist perturbation by pressure in the experimentally available range.

Several related observations deserve mention herein. Below the transformation pressure, the cerium was often partially converted to an alternative form (tentatively identified as a close-packed hexagonal form) which occasionally persisted even at the highest pressures. In view of the lack of reproducibility in the formation of this phase, we believe it to be a metastable form created by the action of unavoidable but variable friction transmitted by the binding cement. Upon sudden release of the high pressure, this form (unmistakably identifiable as close-packed hexagonal) invariably was present and gradually transformed over a period of days to the original face-centered cubic modification. After several weeks the cerium oxidizes and only CeO<sub>2</sub> lines are observed in the diffraction pattern.

In agreement with Bridgman,<sup>4</sup> we observe that below the transformation pressure the compressibility of Ce progressively increases with increasing pressure, accounting for an appreciable fraction (over  $\frac{1}{3}$ ) of the over-all volume change. We believe that this progressive increase in compressibility, terminating in a decisive collapse, is responsible for an increase in amplitude of thermal vibration in the lattice and accordingly explains the anomalous increase of resistance with pressure in Ce, previously reported by Bridgman.<sup>3</sup>

Attempts to produce the transformation in rather impure Ce (containing at least 0.2 percent Fe) existing in the hexagonal modification at atmospheric pressure were unsuccessful.

\* This research was supported in part by the ONR under Contract ori-6-20-XX.

<sup>1</sup> A. W. Hull, *Phys. Rev.* **18**, 88 (1921).  
<sup>2</sup> L. I. Quill, *Zeits. f. anorg. allgem. Chem.* **208**, 273 (1932).  
<sup>3</sup> P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, Ltd., London, 1931).  
<sup>4</sup> P. W. Bridgman, *Proc. Am. Acad.* **76**, 55 (1948).  
<sup>5</sup> F. Trombe and M. Foex, *Ann. d. Chem.* **19**, 417 (1944).  
<sup>6</sup> F. Trombe, *Comptes Rendus* **198**, 1591 (1934).

<sup>7</sup> The authors are indebted to Professor Norman Nachtrieb for performing the chemical analyses.

<sup>8</sup> To be described elsewhere.

<sup>9</sup> Private communication.

<sup>10</sup> C. H. La Blanchetals, *Comptes Rendus* **220**, 392 (1945).

## The Frequency $\nu_2$ in the Infra-Red Spectrum of CH<sub>4</sub>

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May 27, 1949

THE infra-red spectrum of methane has been investigated at length by Cooley<sup>1</sup> and Nielsen and Nielsen,<sup>2</sup> and the complex structure of the band  $\nu_4$  has been admirably analyzed by Jahn<sup>3</sup> and Childs and Jahn<sup>4</sup> in a series of papers. They accounted for the rotational structure of  $\nu_4$  on the basis that there exists a resonance Coriolis interaction between the frequency  $\nu_4$  and the optically inactive frequency,  $\nu_2$ . This analysis has been verified by Shaffer, Nielsen, and Thomas<sup>5</sup> who have presented a theory of the rotation-vibration problem of the tetrahedrally symmetric XY<sub>4</sub> type of molecule complete to second order of approximation.

The Coriolis interaction affects the vibrations somewhat in the following manner. If  $\nu_4$  is larger than  $\nu_2$ , the effective moments of inertia in these states will be, respectively, larger and smaller than the moment of inertia in the normal vibrational state. This should give rise to convergence of the rotational lines in  $\nu_4$  toward higher frequencies, and in the frequency  $\nu_2$ , if it were active, toward lesser frequencies. If, on the other hand,  $\nu_4$  is smaller than  $\nu_2$ , a situation just the reverse of the above should prevail.

The Coriolis perturbation will cause a mixing of the wave functions of the two states so that, if the two frequencies are near enough alike, it should be possible to observe  $\nu_2$ . This is indeed the case in the molecules SiH<sub>4</sub> and GeH<sub>4</sub>, where the two frequencies are separated by 65 cm<sup>-1</sup> and 114 cm<sup>-1</sup>, respectively. Tindal, Straley, and Nielsen<sup>6</sup> have reported on the activity of the band  $\nu_2$ , induced by this Coriolis interaction, for these two molecules. The frequency  $\nu_2$  has never been observed in the spectrum of CH<sub>4</sub>, principally because it overlaps almost exactly the region of the strong water vapor band. An indication of its existence is nevertheless suggested by the data of Coblenz.<sup>7</sup>

This region has been explored with our vacuum infra-red grating spectrometer, and the band  $\nu_2$  has now been observed. The band center has been determined to lie at about 1533.6 cm<sup>-1</sup> while  $\nu_4$  lies at 1305.9 cm<sup>-1</sup>. The Q branches of these two bands do fold away from each other as is to be expected from the theory outlined above, and the  $\nu_2$  band is considerably weaker in intensity.

Complete details of these measurements will be published at a later date.

<sup>1</sup> J. P. Cooley, *Astrophys. J.* **62**, 73 (1925).

<sup>2</sup> A. H. Nielsen and H. H. Nielsen, *Phys. Rev.* **48**, 864 (1935).

<sup>3</sup> H. A. Jahn, *Proc. Roy. Soc. London* **168A**, 469, 495 (1938).

<sup>4</sup> W. H. J. Childs and H. A. Jahn, *Proc. Roy. Soc. London* **169A**, 451 (1939).

<sup>5</sup> Shaffer, Nielsen, and Thomas, *Phys. Rev.* **56**, 895, 1051 (1939).

<sup>6</sup> Tindal, Straley, and Nielsen, *Phys. Rev.* **62**, 151, 161 (1942).

<sup>7</sup> W. W. Coblenz, *Pub. Carnegie Inst. Wash.*, D. C. **I**, 43 (1905).

## Note on Measurements of Ambipolar Diffusion in Helium\*

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June 3, 1949

THE discussion presented in the last paragraph of the article "Measurements of ambipolar diffusion in helium"<sup>1</sup> is in error. The mobility of He<sup>++</sup> should be  $\sqrt{2}$  times the mobility of He<sup>+</sup> if charge transfer is neglected, and thus would not explain the difference between our measurements and those of Tyndall and Powell. Meyerott<sup>2</sup> has suggested that the theoretical mobility of