

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,  $CeO_2$  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  $1.85 \pm 0.01 \text{ \AA}$  and  $1.71 \pm 0.02 \text{ \AA}$ , respectively; the lattice constants observed correspond to ionic radii of  $1.82 \text{ \AA}$  and  $1.71 \pm 0.02 \text{ \AA}$  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  $CeO_2$  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.

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<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 $CH_4$

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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  $XY_4$  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  $SiH_4$  and  $GeH_4$  where the two frequencies are separated by  $65 \text{ cm}^{-1}$  and  $114 \text{ cm}^{-1}$ , 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  $CH_4$ , 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  $1533.6 \text{ cm}^{-1}$  while  $\nu_4$  lies at  $1305.9 \text{ cm}^{-1}$ . 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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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  $He^{++}$  should be  $\sqrt{2}$  times the mobility of  $He^+$  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