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Crystal Structure of Lanthanum Nitride^{1,2}

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Lanthanum nitride has been prepared by direct combination between lanthanum metal and nitrogen to yield a product having approximately the composition LaN. The crystal structure of LaN has been shown to be of the NaCl type, confirming the earlier work of Iandelli and Botti.³ The powder X-ray diffraction patterns of LaN and face-centered cubic lanthanum metal have been shown to be demonstrably different. The dissociation pressure of LaN was found to be very small at 900°. The lanthanum nitride specimens gave no evidence of superconductivity down to 1.8°K.

During the course of a study of the occurrence of superconductivity in compounds it became of interest to examine lanthanum nitride for possible superconductivity. This substance has been reported³ to have the NaCl-type structure, but no data were given for the chemical composition of the substance examined. It is the purpose of the present paper to report on the crystal structure of several specimens prepared under carefully controlled conditions. Two different specimens were examined for superconductivity, using a magnetic method similar to that employed by Horn and Ziegler.⁴ No evidence of superconductivity was found down to 1.8° K., the lowest temperature used. The details of the low temperature experiments will be reported in another place.

Preparation of Lanthanum Nitride

The lanthanum nitride specimens were prepared by a modification of the direct combination-method described by Muthmann and Kraft,⁵ since this method appeared most likely to yield a pure product.

The nitriding apparatus consisted of a quartz tube vacuum furnace, connected to a high vacuum oil diffusion pump. The apparatus was also equipped with a 100-ml. water-jacketed mercury-filled gas buret, by means of which a known amount of dry nitrogen could be introduced into the system. Proper manipulation of the buret permitted the pressure of the nitrogen in the furnace to be maintained at about one atmosphere during nitrogen absorption, and also permitted the rate of nitrogen absorption to be followed. The nitrogen remaining after completion of the reaction could be removed by means of a Toepler pump and its volume determined.

The reaction was carried out using several tenths of a gram of lanthanum-filings prepared from the bulk metal by filing in a dry helium or nitrogen atmosphere. In a preliminary experiment it was ascertained that filings exposed for six days to dry nitrogen at room temperature showed no weight increase within experimental error (equivalent to 1.5 atomic % nitrogen). Molybdenum combustion boats were used, copper boats having been found to be unsatisfactory. The dry nitrogen used was a special grade obtained from the Air Reduction Company stated to contain 0.10% oxygen. It was passed over copper at 600° and through a liquid nitrogen trap before being metered into the furnace.

The lanthanum used was obtained from two sources. Specimen A (Table I) was obtained from Cooper Metallurgical Associates, Cleveland, Ohio. It was analyzed by spectrographic and spectrophotometric methods, by direct precipitation as the oxalate and by ion-exchange techniques. Consideration of the results obtained by these methods led to the figure 97.5% lanthanum as being representative of the rare earth content; of this 1.1% was cerium, 0.4% neodymium, 0.2% praseodymium and 0.2% other rare earths. The metal also contained about 0.7% silicon, 0.8% iron and some carbon.

Specimen B was obtained from Dr. F. H. Spedding, Iowa State College, Ames, Iowa. Spectrographic analysis showed that it contained 0.13% beryllium, 0.1% magnesium, traces of calcium, aluminum, and iron and was free of other rare earths. Direct precipitation as the oxalate gave a lanthanum content of 97.3%. However, in view of the high purity of this material the lanthanum content has been arbitrarily taken to be 100%.

No chemical analyses of the lanthanum specimens for carbon, nitrogen, oxygen or hydrogen were made. The presence of carbon was inferred from the acetylene-like odor (more pronounced in the Cooper specimen) given off when the filings were dissolved in dilute hydrochloric acid. However, X-ray diffraction analysis of the metal filings showed that all except a few very faint lines were assignable to either a cubic close-packed or hexagonal close-packed lanthanum structure.

The calculation of x in the formula LaN_x was based on these lanthanum contents. Cerium, praseodymium and neodymium have also been reported to form nitrides with the approximate formula MN.^{3,6}

The reaction was carried out as follows. A weighed amount of filings was degassed by pumping at 10⁻⁶ mm. for several hours at room temperature. The nitrogen gas was then admitted, and the electric furnace turned on. After about one hour the furnace temperature had risen to 600° at which temperature the reaction began. The reaction proceeded to approximate completion in two to four hours at 750° and in one to two hours at 900°. The reaction chamber was usually kept at 900° for about 20 hours to ensure complete reaction. After cooling to room temperature (the pressure being maintained at approximately one atmosphere by suitable manipulation of the mercury level in the buret) the nitrogen remaining was determined volumetrically and the reaction product was weighed.

The lanthanum filings and nitride products were always handled in such a manner as to protect them from contact with air, since both materials react with moist air.

The details of the several preparations are shown in Table I. The results corresponded rather closely to the formula LaN, although the value of x in the formula LaN_x was in all instances somewhat less than unity. The presence of several per cent. of lanthanum carbide, oxide, nitride or hydride in the metal could account in part for this discrepancy.

The over-all accuracy of the volume measurements was estimated to be about 1%, based on separate control experiments. Weights were reproducible to ±0.3 mg. It will be noted that the values of x calculated from the volumetric measurements were 4 to 8% smaller than the gravimetric values. The reason for this is not clear. Desorption of gases from the specimen and the apparatus would appear to be ruled out since in Expt. 25 the metal filings were heated in a high vacuum for four hours at 600°, cooled in helium and reweighed before nitriding. The observed change in weight was 0.1 mg. The evolution of hydrogen gas at 900° from any lanthanum hydride present in the metal filings might account for the discrepancy, since the hydride is known (unpublished results by us) to decompose at 700° in a high vacuum.

The lanthanum nitride products were loose black powders which liberated ammonia on exposure to air, in agreement with the observations of Muthmann and Kraft⁵ and Neumann, *et al.*⁷ However, the nitridation reaction was found

(1) This work was carried out with the assistance of the Office of Naval Research under Contract N6-ori-192.

(2) From the M.S. thesis in physics of R. A. Young, December, 1950.

(3) A. Iandelli and E. Botti, *Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*, **25**, 129 (1937).

(4) F. H. Horn and W. T. Ziegler, *THIS JOURNAL*, **69**, 2762 (1947).

(5) W. Muthmann and K. Kraft, *Ann.*, **325**, 262 (1902).

(6) A. Iandelli and E. Botti, *Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*, **25**, 638 (1937).

(7) B. Neumann, C. Kroeger and H. Kunz, *Z. anorg. u. allgem. Chem.*, **207**, 133 (1932).

TABLE I
NITRIDATION OF LANTHANUM METAL
A = Cooper, 97.5% La; B = Spedding, 100% La

| Expt. no. | Source | Metal filings, wt., mg. | Nitrogen absorbed, mg. | Wt. increase | Nitrogen absorbed, ml. (N.T.P.) | Volume meas. | Wt. increase | Volume meas. | Experimental conditions ^a |
|-----------|--------|-------------------------|------------------------|--------------|---------------------------------|--------------|--------------|-------------------------------|--------------------------------------|
| 23 | A | 333.6 | 30.0 | 24.1 | 21.9 | 0.92 | 0.84 | 5 hr. at 900° | |
| 25 | A | 415.7 | 38.8 | 31.0 | 29.6 | .97 | .93 | 17 hr. at 750 3 hr. at 920 | |
| 26 | A | 424.0 | 41.3 | 33.1 | 31.4 | .99 | .95 | | |
| 29 | B | 562.6 | 55.9 | 44.7 | 41.0 | .97 | .91 | 20 hr. at 900 | |

^a Temp. in °C., nitrogen pressure, 1 atm.

to proceed quite briskly at temperatures more than 100° below those employed by these investigators.

The dissociation pressure of lanthanum nitride was investigated briefly. The product of Expt. 23 was heated in a high vacuum (*ca.* 5×10^{-6} mm.) for five hours at 900° with no detectable loss in weight. It would appear that the dissociation pressure of lanthanum nitride is extremely small even at 900°. It seems unlikely, therefore, that the composition of the products was significantly affected by small changes in the nitrogen pressure during preparation.

Determination of Crystal Structure

Iandelli and Botti³ have examined the crystal structure of lanthanum nitride prepared by the direct combination method, but did not give the composition of their nitride. From powder X-ray diffraction data, they reported that lanthanum nitride has an NaCl-type structure with $a_0 = 5.27_6$ Å. (probably actually kx. units). The results of the present investigation are in general agreement with their work.

In the present investigation both the lattice parameter and the structure type of three of the samples (those from Expts. 25, 26, 29) described in Table I were determined using the powder method of X-ray diffraction. A 14.32-cm. diameter Debye-Scherrer type camera was used, with filtered $\text{CuK}\alpha$ radiation. Specimens were contained in Pyrex capillaries which were filled in a "dry-box" in an inert (helium or nitrogen) atmosphere, and sealed in a flame within 15 seconds after removal from the "dry-box."

Films used for lattice parameter determinations were calibrated by the septum technique.⁸ By using both copper and silver as standard substances it was shown that, within the limit of experimental error, no correction need be applied to the observed line positions to take account of the differing absorption coefficients. Two calibrated films were obtained with each of the nitride products from Expt. 25 and 26 and one film from the nitride product of Expt. 29.

The relative intensities of the lines were determined on films obtained without the use of a septum. Approximate integrated intensities were determined by multiplication of a number roughly proportional to the exposure⁹ by a number representing the approximate width of the line. Where K_{α_1} and K_{α_2} were resolved the intensities were added to obtain the intensity for that reflection. By this means the observed relative line intensities were represented by numbers which could be normalized and averaged over several films. Typical powder data for lanthanum nitride are given in Table II.

The pattern of lanthanum nitride is immediately recognizable as being due to a face-centered cubic (f.c.c.) crystal by the 2-1-2-1-2 grouping of the lines. The average a_0 obtained from the five calibrated films was 5.284 ± 0.004 kx. units (5.295 ± 0.004 Å.), in fair agreement with the value 5.27_6 kx. units reported by Iandelli and Botti.

In determining the crystal structure three types of face-centered cubic structures were considered: NaCl, ZnS and a random type in which the nitro-

(8) Although some non-uniform film shrinkage was detected in this way, it was not sufficient to warrant departure from a straight line calibration curve such as would be obtained with the Straumanis technique.

(9) This number was the time in seconds required to produce the same darkening (as judged visually) on a separate piece of the same X-ray film, using the beam from the same X-ray tube and an appropriate absorber.

TABLE II
TYPICAL POWDER DATA FOR LANTHANUM NITRIDE^a

| <i>hkl</i> | <i>d</i> , kx. units | Relative intensity |
|-------------|----------------------|--------------------|
| 111 | 3.05 | 24 |
| 200 | 2.64 | 22 |
| 220 | 1.87 | 36 |
| 311 | 1.59 | 45 |
| 222 | 1.52 | 24 |
| 400 | 1.32 | 13 |
| 331 | 1.21 | 34 |
| 420 | 1.18 | 45 |
| 422 | 1.078 | 44 |
| 511 and 333 | 1.017 | 48 |
| 440 | 0.934 | 22 |
| 531 | .894 | 77 |
| 600 and 442 | .881 | 59 |
| 620 | .836 | 70 |
| 533 | .806 | 80 |
| 622 | .798 | 100 |

^a Sample from Exp. 26 (Film 16-235).

gen atoms were assumed to replace lanthanum in the f.c.c. lattice. This last type, while perhaps unlikely, was considered worthy of investigation because the reported a_0 for f.c.c. lanthanum is almost identical with the value obtained here for the nitride. It was assumed that the relative intensities of the lines for such a random type would be the same as for f.c.c. lanthanum.

The expected relative line intensities, I , were calculated for each type by the relation

$$I \sim F^2 p U \frac{1 + \cos^2 2\theta}{\sin 2\theta \sin \theta}$$

where

I = relative intensity of the diffracted line

F = the crystal structure factor

p = the multiplicity of the "reflection"

θ = the Bragg angle of the diffracted line

U = the appropriate absorption factor as obtained from a plot of the values listed by Rusterholtz¹⁰ for the case of large absorption in a cylindrical sample

The relative line intensities to be expected for the three structure types would not be expected to differ very much, as the scattering power of nitrogen is much smaller than that of lanthanum. Indeed, a line by line comparison between the observed relative intensities and those for the three calculated sets did not permit a clear-cut decision in favor of any one type, though the agreement between the observed intensities and those calculated for the NaCl-type structure appeared to be

(10) A. Rusterholtz, *Z. Physik.*, **63**, 1 (1930).

somewhat better than for the other two types. In order to examine this agreement more critically the relative intensities were replotted as ratios of the intensity of each line in a set to the intensity of the line with next larger θ . These data are given in Table III.

TABLE III
INTENSITY RATIOS

| Miller indices of lines involved | Theoretical ratios of LaN | | | Average observed ratios | | |
|--|---------------------------|----------|--------------------------|-------------------------|--------------------|------------------------|
| | NaCl type | ZnS type | Random type ^a | LaN ratio | LaN mean deviation | f.c.c. La ^b |
| 111/200 | 1.05 | 1.91 | 1.51 | 1.06 | 0.04 | 1.80 |
| 200/220 | 0.72 | 0.49 | 0.71 | 0.65 | .10 | 0.61 |
| 220/311 | 0.81 | 0.69 | 0.59 | 0.74 | .02 | .54 |
| 311/222 | 2.42 | 3.86 | 3.27 | 1.99 | .28 | 3.19 |
| 222/400 | 1.54 | 1.13 | 1.53 | 1.81 | .13 | 1.66 |
| 400/331 | 0.36 | 0.31 | 0.27 | 0.39 | .01 | 0.31 |
| 331/420 | 0.78 | 1.18 | 1.02 | 0.78 | .05 | 0.97 |
| 420/422 | 1.03 | 0.78 | 1.01 | 1.03 | .10 | 1.34 |
| 422/ ⁽⁵¹¹⁾ ₍₃₃₃₎ | 0.94 | 0.81 | 0.73 | 0.90 | .01 | 0.71 |
| ⁽⁵¹¹⁾ ₍₃₃₃₎ /440 | 1.78 | 2.05 | 2.30 | 2.21 | .17 | 2.70 |
| 440/531 | 0.26 | 0.23 | 0.21 | 0.28 | .02 | 0.28 |
| 531/ ⁽⁶⁰⁰⁾ ₍₄₄₂₎ | 1.17 | 1.71 | 1.49 | 1.26 | .04 | 1.53 |
| ⁽⁶⁰⁰⁾ ₍₄₄₂₎ /620 | 0.89 | 0.69 | 0.89 | 0.88 | .08 | 0.98 |
| 620/533 | .87 | .76 | .67 | .89 | .10 | .80 |
| 533/622 | .66 | .97 | .86 | .80 | .10 | .75 |

^a Same as f.c.c. lanthanum metal. ^b Observed for f.c.c. modification of lanthanum metal.

Examination of the data in Table III shows that the observed intensity ratios are most nearly in agreement with those calculated for the NaCl type. It was concluded, therefore, that lanthanum nitride has this crystal structure. This is in agreement with the result reported by Iandelli and Botti.^{3,11} However, these investigators did not consider any random types, and seemingly made a slight error in the calculation of the relative intensities for the ZnS type.¹²

It is interesting to note that, as Iandelli and

(11) A preliminary study of a sample of cerium nitride prepared under similar conditions and having the formula CeN_{0.87} showed this nitride to have a f.c.c. structure with $a_0 = 5.01$ kx. units, in good agreement with the observation of Iandelli and Botti.³

(12) A. Iandelli and E. Botti, *Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*, **24**, 465 (1936).

Botti³ have pointed out, lanthanum nitride and the f.c.c. modification of lanthanum have very nearly identical values of a_0 . Thus, a specimen of f.c.c. lanthanum prepared by heat treatment¹³ at 350° for four days showed an a_0 of 5.291 ± 0.003 kx. units, compared to 5.284 ± 0.004 kx. units for the nitride. Because of this fact the X-ray method used here can give no information about the presence of free lanthanum metal in the lanthanum nitride. More precise measurements are planned with a Geiger counter spectrometer.

Rossi¹⁴ noted that the f.c.c. modification of lanthanum seemed to be only a surface effect. Iandelli and Botti³ suggested that, since the lattice parameters were the same, the pattern previously ascribed to f.c.c. lanthanum might actually be due to a surface formation of lanthanum nitride. These suggestions were investigated (1) by visually comparing a large number of films registering the pattern from a material believed to be f.c.c. lanthanum with the films from the nitride samples and (2) by measuring and comparing the observed relative intensities of the f.c.c. lanthanum films in the same way that comparisons were made for the nitride. The data for the quantitative comparisons are also listed in Table III. The comparisons showed that f.c.c. lanthanum yields a powder diffraction pattern having relative line intensities that are detectably, although slightly, different from those of the nitride pattern. The most obvious difference, which may be seen at a glance, occurs in the relative intensities of the first two lines of the patterns. The data also show that the observed relative intensities for f.c.c. lanthanum agree better with those calculated for f.c.c. lanthanum than with those calculated for either NaCl or the ZnS-type nitride.

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(13) See E. Zintl and S. Neumayr, *Z. Elektrochem.*, **39**, 84 (1933).

(14) A. Rossi, *Nature*, **133**, 174 (1934).