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NUCLEAR QUADRUPOLE RESONANCE IN $TiCl_4$, $ThCl_4$, $NbCl_5$, $TaCl_5$

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Allan H. Reddoch

November 4, 1960

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ABSTRACT

The chlorine resonance in titanium tetrachloride has been re-examined, confirming the existence of four resonances.

A chlorine-35 resonance at about 6 Mc has been discovered in thorium tetrachloride. The frequency suggests highly ionic bonding, which contradicts earlier conclusions from x-ray studies. Some double-bond character may be present in the Th-Cl bond.

Niobium and chlorine resonances have been discovered in niobium pentachloride. The niobium resonances are described by a single set of parameters, the coupling constant eQq being approximately 78 Mc, and the asymmetry parameter, $\eta = 0.32$. Because of the large asymmetry parameter, it was possible to observe two $\Delta M = 2$ and one $\Delta M = 3$ transitions. Only a single Cl^{35} resonance was found at about 13 Mc, although two more chlorine resonances would be expected on the basis of crystal structure. The frequency of the chlorine resonance suggests appreciable covalency in the niobium-chlorine bond in niobium pentachloride.

A single resonance has been found in tantalum pentachloride at about 13 Mc. It is believed to be a chlorine-35 resonance.

A fairly simple method is outlined for determining the asymmetry parameter of the electric-field gradient from the observed transition frequencies without directly solving the secular equations.

NUCLEAR QUADRUPOLE RESONANCE

in TiCl_4 , ThCl_4 , NbCl_5 , and TaCl_5^* Allan H. Reddoch[†]Lawrence Radiation Laboratory and Department of Chemistry
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November 4, 1960

I. INTRODUCTION

The theory of nuclear quadrupole resonance has shown that the resonance frequencies can give information concerning the chemical bonds in the sample as well as information relating to the structure of the lattice.¹

Thorium chloride was investigated in order to study the nature of the bonds in the compounds. The spectrum of TiCl_4 was reinvestigated to test the equipment and to serve as a model of fairly ionic compounds. Other Group IV and V chlorine compounds were studied to get a better picture of such ionic compounds.

II. EXPERIMENTAL PROCEDURE

Most of the measurements below 13 Mc/sec were made using a circuit similar to that of Pound and Watkins.² At higher frequencies a self-quenched superregenerative circuit based on Dean's design was used.¹ A phase-sensitive detector similar to Watkins's circuit was employed.

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Zeeman modulation was used, the magnetic field consisting of square pulses of alternating polarity with a frequency of about 100 cps and an amplitude of about 15 gauss.

Resonant frequencies were measured with a General Radio Company military-type heterodyne frequency meter (model LR). Frequency comparisons were made as the resonance was recorded. The average of values obtained with the frequency increasing and decreasing was used to avoid errors arising from the time constant of the filter circuit. Checks for internal consistency, estimates of possible systematic errors, and comparison with reported frequencies suggest that the present measurements should be accurate to within 0.3 kc/sec.

When the superregenerative spectrometer was used, frequency measurements were made at different quench frequencies in order to distinguish the central line from the sidebands. However it was found that with the self-quenched circuit, this procedure was not infallible, because the quench-frequency adjustment sometimes changed the central radio frequency sufficiently to yield an ambiguous result.

Room temperatures were measured with a mercury thermometer and should be accurate to 0.1°C. The low temperatures were measured with a thermocouple and should be accurate to 0.5°C. However, the relative accuracy of individual temperatures at either dry-ice or liquid-nitrogen temperatures should be about 0.1°C.

The samples usually consisted of 5 to 10g of polycrystalline material in a sealed tube. The coils of the oscillator tank circuit were wound directly on the sample tube.

Further details are given elsewhere.³

III. RESULTS AND DISCUSSION

A. Titanium Tetrachloride

The chlorine resonance in titanium tetrachloride has been reported previously by Dehmelt⁴ and by Hamlen and Koski.⁵ The latter workers could see only three of the four lines reported by Dehmelt, possibly because the sidebands of their superregenerative spectrometer obscured the details of the spectrum. The present results, obtained with a marginal oscillator, show four lines very clearly (Fig. 1). The frequencies of these lines are given in Table I. The lines are about 2.5 kc/sec wide and appear to be of equal intensity. The temperature dependence is normal.

A number of other tetrahalides, including SiCl_4 , GeCl_4 , SnCl_4 , and SnBr_4 , have spectra consisting of four lines.^{6,7} The spectra of these compounds show three lines close together with a fourth line at a somewhat lower frequency. It has been suggested that the similarity of the spectra indicates a common crystal structure.^{6,8} The detailed structure of these compounds is not known although Shimomura has concluded that the quadrupole spectrum of SnBr_4 is the result of a tetrahedral molecule in a monoclinic lattice.⁸

Although the spectrum of TiCl_4 does not show any significant splitting into a singlet and triplet, it seems quite possible that TiCl_4 has the same crystal structure as the other tetrahalides having four-line spectra. The lower frequency of the resonance and the presumably greater ionicity of TiCl_4 may tend to change the structure of the spectrum. The physical properties of these tetrahalides, the ionic radii, and the common crystal structure (SnI_4) of the heavier tetrahalides of Ti and other Group-IV elements are all consistent with a common crystal structure for the corresponding lighter tetrahalides.

B. Thorium Tetrachloride

A sample of ThCl_4 was prepared by the direct reaction of chlorine with high-purity thorium metal at 400°C , followed by sublimation of the product. The sample was protected from oxygen and water vapor at all times.

The chlorine spectrum consists of a single line for each isotope, as would be expected from the crystal structure. The frequencies at several temperatures are given in Table II. The signal-to-noise ratio increased with decreasing temperature, and only at low temperatures was it possible to measure accurately the frequency of the weaker Cl^{37} line. The ratio of the frequencies of the two isotopes (1.2688) agrees well with similar ratios reported elsewhere (1.2685 to 1.2690)⁹ and supports the assignment of the resonances and the accuracy of the measurements.

The theory of Townes and Dailey yields an estimate of 87% for the ionicity of the Th-Cl bond, if 15% s-hybridization of the chlorine orbitals is assumed. The generally accepted value of 1.4 for the electronegativity of thorium¹⁰ gives a point that lies very close to the curve of Townes and Dailey relating ionicity and electronegativity (Fig. 2). The value of 1.6 for the thorium electronegativity recently proposed by Fineman and Daignault¹¹ moves the point to the left, so that it is now above the curve. The bond could then be assigned the ionicity predicted by the curve (74%) and the deviation from the curve could be ascribed to 22% π character.

In any case, the Th-Cl bond seems to be quite ionic. This conclusion does not support the statement by Zachariasen¹², based on crystal structure, that the bond is predominantly covalent. The flattened tetrahedron found in the crystal is not a simple coordination structure and undoubtedly reflects some covalency. However, it appears that a small amount of covalent character may have an appreciable effect on the bond angles in the crystal.

The physical properties of TiCl_4 and ThCl_4 are quite different in spite of the similarity of their resonant frequencies and ionicities. The differences may arise from different molecular structures in the crystals. If TiCl_4 remains a regular tetrahedron in the solid, it may be described as "shielded".¹³ In other words the symmetric arrangement of large chlorine ions around the titanium ion tends to neutralize the charge of the latter as far as other external ions are concerned. External charges are also kept some distance from the titanium ion. Thus while there may be strong intramolecular ionic forces, the intermolecular forces are weak. The compound is similar to covalent compounds in having a low melting point. While low temperatures can disrupt the intermolecular bonds, it cannot break the strong intramolecular bonds, and thus the compound has no electrical conductivity at the melting point.

In ThCl_4 the flattened tetrahedra permit fairly strong intermolecular ionic forces. The compound has a fairly high melting point. The melting temperature is high enough to break some of the intramolecular bonds and the compound has a moderate electrical conductivity at the melting point.

The most striking feature of the resonance in ThCl_4 is the temperature dependence. Most compounds have a temperature coefficient of about $-10^{-4}/^\circ\text{C}$. For ThCl_4 , the frequency has a maximum in the region of -50°C , and the maximum coefficient in the range studied is about $4 \times 10^{-6}/^\circ\text{C}$. This behavior is similar to that reported for TiBr_4 .¹⁴ For WCl_6 the temperature coefficient is positive, having a value of $2 \times 10^{-4}/^\circ\text{C}$.⁵

In a plot of ionicity against electronegativity the point for WCl_6 lies appreciably above the curve of Townes and Dailey as does the point for TiBr_4 . If the value of 1.6 is used for the thorium electronegativity, ThCl_4 also lies above the curve.

Such deviations may be ascribed to partial π bonding in these compounds. Such π bonding would permit an explanation of the temperature

coefficients of these compounds. As the bonds lengthen with increasing temperature, the π character should decrease. Such a decrease would cause the resonant frequency to rise. At the same time, the factors that tend to decrease the frequency, such as torsional oscillations, would be operating. The net temperature coefficient would be the difference between these effects and would depend on the relative magnitude of the effects. A rough calculation based on the relation between bond order and bond lengths gives the right order of magnitude. The effect is similar to that proposed by Oka^{15, 16} and coworkers to explain the increased halogen coupling constants in the higher vibrational states of ICN and BrCN.

The recent observation of quadrupole resonance in paramagnetic compounds by Barnes and Segel¹⁷ suggests that it may be possible to find a chlorine resonance in UCl_4 analogous to that found in ThCl_4 , since the compounds are isomorphous and have similar properties.

C. Niobium Pentachloride

In NbCl_5 , resonances may be expected from Nb^{93} as well as from the two chlorine isotopes. Since Nb^{93} has a spin of $9/2$, at least four lines may be expected from this nucleus. The observed resonances are listed in Table III together with their assignments and the calculated values of the niobium frequencies. The calculated values were obtained from the secular equation for $I = 9/2$. The two parameters were obtained by a least-squares fitting to the four principal frequencies. The agreement between the observed and calculated frequencies is quite good and supports the assignment of the transitions.

If a small correction is applied for the difference in temperature between the two room-temperature measurements of the chlorine frequencies, the frequency ratio is found to be 1.2688. This value supports the assignment of these lines to the chlorine isotopes.

No quantitative measurements were made of the niobium intensities but qualitatively the intensities follow the pattern expected from the assignment of the resonances. The chlorine lines are about 2 kc/sec wide while the the four main niobium lines are about 7 kc/sec wide. The other three niobium lines appear to be 10 to 20 kc/sec wide.

Zalkin and Sands have shown that NbCl_5 in the solid forms dimeric $\text{Nb}_2\text{Cl}_{10}$ units (Fig. 3).¹⁸ The niobium atoms are at the centers of two adjacent distorted octahedra of chlorine atoms. The octahedra share a common edge. The dimer contains two equivalent niobium atoms and three nonequivalent sets of chlorine atoms, two bridging chlorine atoms between the niobiums, four more chlorines in the same plane, and four more above and below the plane. The authors state that the molecules occupy lattice sites having two different symmetries, but that all the molecules appear to be identical.

From this structure, one resonance would be expected from the niobium while three resonances would be expected from the chlorines, the one from the bridging chlorines probably being separated from the other two. If the molecules at the two lattice sites were not completely equivalent, some doubling of these resonances might occur.

The absence of any doubling is consistent with all the molecules being equivalent. The 2 kc/sec width of the chlorine line at 13 Mc/sec precludes any splitting in frequency of more than one in 10^4 . Presumably the dimensions of the molecules would not differ by much more than this order of magnitude.

The failure to find more than one chlorine resonance is quite puzzling. Searches were made from 2.5 to 40 Mc/sec. The observation of the weak niobium line at 21 Mc/sec indicates that considerable sensitivity was available.

The observed chlorine resonance may arise from the two bridging chlorines, because the remaining chlorines ought to give a pair of resonances which are fairly close together in frequency and similar in intensity.

The tentative assignment of the observed chlorine resonances and the absence of the others make it difficult to give a chemical interpretation of the results.

The frequency of the chlorine resonance suggests appreciable ionicity as well as covalency. However a purely ionic model in which the ions have point charges of +5 and -1 gives values of eQ and η for the niobium resonance which are two or three times too small. The calculation was quite crude, because only the six nearest chlorines and one nearest niobium were considered.

Murakawa found a coupling constant of 0.15 Mc/sec for the ground state of the Nb^{93} atom ($4d^4 5s$) and 0.09 Mc/sec for the excited state ($4d^3 5s^2$).¹⁹ His values are much lower than the value found here for $NbCl_5$ and are probably the result of the nonpenetrating character of the d orbitals. In the compound, the bonding orbitals are probably s-p-d hybrids. Such orbitals can have large coupling constants because of the penetrating nature of the p components, which give contributions to the field gradient q of the form $\langle p|q|p \rangle$, and because of cross terms of the form $\langle s|q|d \rangle$, which can also be large.

The non zero asymmetry parameter indicates a lack of axial symmetry at the niobium. Hence the nuclear eigenstates are mixtures of the spin states and under the selection rule $\Delta M = 0, \pm 1$ transitions are possible between any pair of states.

As in the work of Cohen,²⁰ the relative intensities of the transitions were calculated. The $\pm 9/2$ states do not mix appreciably, and so the transitions to the $5/2$, $3/2$, and $1/2$ states were too weak to observe here. All

the other transitions were seen with the superregenerative spectrometer and qualitatively have the expected intensities. With the Pound-Watkins circuit, only the four main transitions and the $1/2 \rightarrow 5/2$ transition could be seen.

Molybdenum chloride, MoCl_5 , has the same crystal structure as NbCl_5 ;²¹ however it is paramagnetic. It might be possible to examine the chlorine resonances in this compound.

D. Tantalum Pentachloride

Tantalum pentachloride is thought to have the same crystal structure as niobium pentachloride.¹⁸ The chemical and physical properties of the two compounds are similar. A single weak resonance was found at 13.391 Mc/sec at 24.3°C. No other lines were found up to 25 Mc/sec.

Tantalum has a very large quadrupole moment. If the field gradients due to the chlorines were similar in TaCl_5 and NbCl_5 , the tantalum resonances would have frequencies of 100 to 200 Mc/sec. The present equipment did not operate in this range.

The observed resonance must be a chlorine line and probably arises from Cl^{35} . A weaker line from Cl^{37} should occur at 10.5 Mc/sec. It was not seen, probably because it was too weak. If the observed line came from Cl^{37} , a fairly strong line would be expected at 16.8 Mc/sec, and its absence would be difficult to understand.

The observed line seems to correspond to the chlorine resonance at 13.058 Mc/sec in NbCl_5 and illustrates the chemical similarity of the Ta and Nb compounds. The failure to observe other chlorine lines in TaCl_5 corresponds to the situation in NbCl_5 .

E. Miscellaneous

Niobium oxychloride (NbOCl_3)²² has some structural features in common with NbCl_5 . For this reason an attempt was made to find resonances in the compound. No resonances were found between 5.3 and 38.3 Mc/sec. However the sample was not very large (2 gm), and the failure may not be too significant.

A 13-gm sample of zirconium tetrachloride was examined in order to compare its resonances with those of TiCl_4 and ThCl_4 . No resonances were found between 3.4 and 25.2 Mc/sec.

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APPENDIX: DETERMINATION OF η

Any algebraic equation of the form $\sum_{i=0}^n a_i E^i = 0$, where $a_n = 1$, such as the secular equation for $I = 9/2$, $E^5 - 11(3+\eta^2)E^3 - 44(1-\eta^2)E^2 + \frac{44}{3}(3+\eta^2)^2 E + 48(3+\eta^2)(1-\eta^2) = 0$, may be written in terms of its roots E_j in the form $\prod_{j=1}^n (E - E_j) = 0$. By expanding the latter form and equating the coefficients of like powers of E in the two forms, the following equations, among others, are obtained:

$$\begin{aligned} a_{n-1} &= -\sum E_j \\ a_1 &= (-1)^{n-1} (\prod E_j) \sum \left(\frac{1}{E_j}\right) \\ a_0 &= (-1)^n (\prod E_j). \end{aligned}$$

The observed frequencies are proportional to differences between roots of the secular equation. Thus if the lowest root is called E_0 , the other roots may be written as $E_0 + k\nu_1$, $E_0 + k(\nu_1 + \nu_2)$, etc., where k is a factor containing eQq . For $I = 9/2$, we have $k = h/6A = 24h/eQq$.

Since a_{n-1} equals zero for half-integral spins, the sum of the roots is zero and thus E_0 may be eliminated. Each root E_j may then be expressed as a product of k and an experimental numerical factor. These expressions may be substituted in the equations for a_1 and a_0 above.

Thus for $I = 9/2$ these two equations yield:

$$a_1 = \frac{44}{3}(3+\eta^2)^2 = Nk^4$$

and

$$a_0 = 48(3+\eta^2)(1-\eta^2) = Mk^5,$$

where M and N are numerical factors derived from the observed frequencies.

Elimination of k from these equations yields a numerical value P for the expression $(3+\eta^2)^3/(1-\eta^2)^2 = P$. This equation is fairly easy to solve for η by approximation methods. It is then easy to find k and thus eQq .

The procedure is fairly rapid and quite accurate. For $NbCl_5$ it gave

$$eQq = 78.0812 \text{ Mc/sec}$$

and

$$\eta = 0.32256,$$

while the least-squares procedure based on accurate solutions of the secular equation gave

$$eQq = 78.0809 \text{ Mc/sec}$$

$$\eta = 0.32249.$$

Other coefficients of the secular equation might have been used, but they would require more manipulation. Since the observed frequencies give only approximations to the exact roots, excessive manipulation will probably increase the errors of the resulting estimates of η and eQq .

Any useful pair of coefficients in any of the secular equations for $I = 5/2$, $7/2$, and $9/2$ will yield an equation of the form $(3+\eta^2)^3 = P(1-\eta^2)^2$.

In the course of this work the secular equation for $I = 9/2$ was solved to eight significant figures for 100 equally spaced values of η by using a digital computer. These solutions are given elsewhere.³

REFERENCES

1. T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Solid State Physics series, Supplement I (Academic Press, New York, 1958).
2. G. D. Watkins, An R.F. Spectrometer with Applications to Studies of Nuclear Magnetic Resonances in Solids (thesis), Harvard University, 1952.
3. A. H. Reddoch, Nuclear Quadrupole Resonance of Some Inorganic Chlorine Compounds (thesis), Lawrence Radiation Laboratory Report UCRL 8972, November 1959.
4. H. G. Dehmelt, J. Chem. Phys. 21, 380 (1953).
5. R. P. Hamlen and W. S. Koski, J. Chem. Phys. 25, 360 (1956).
6. A. L. Schawlow, J. Chem. Phys. 22, 1211 (1954).
7. R. Livingston, J. Phys. Chem. 57, 496 (1953).
8. K. Shimomura, J. Sci. Hiroshima University, 17A, 383 (1954).
9. T. C. Wang, Phys. Rev. 99, 566 (1955).
10. W. Gordy and W. J. Orville Thomas, J. Chem. Phys. 24, 439 (1956).
11. M. A. Fineman and R. Daignault, J. Inorg. Nuclear Chem. 10, 205 (1959).
12. W. H. Zachariasen, in The Actinide Elements, G. T. Seaborg and J. J. Katz, Eds., National Nuclear Energy Series, Vol. 14A (McGraw-Hill Book Co., New York, 1954).
13. A. E. Van Arkel, Molecules and Crystals, translated by J. C. Swallow (Butterworths Scientific Publishing Co., London, 1949).
14. R. G. Barnes and R. D. Engardt, J. Chem. Phys. 29, 248 (1958).
15. T. Oka, H. Hirakawa, and A. Miyahara, J. Phys. Soc. Japan 12, 39 (1957).
16. T. Oka and H. Hirakawa, J. Phys. Soc. Japan 12, 820 (1957).

17. R. G. Barnes and S. L. Segel, *Phys. Rev. Letters* 3, 462 (1959).
18. A. Zalkin and D. E. Sands, *Acta Cryst.* 11, 615 (1958).
19. K. Murakawa, *J. Phys. Soc. Japan*, 13, 101 (1958).
20. M. H. Cohen, *Phys. Rev.* 96, 1278 (1954).
21. D. E. Sands and A. Zalkin, *Acta Cryst.* 12, 723 (1959).
22. D. E. Sands, A. Zalkin, and R. E. Elson, *Acta Cryst.* 12, 21 (1959).

Table I. Observed chlorine-35 frequencies in TiCl_4 .

Temperature ($^{\circ}\text{C}$)	Frequencies ^a (Mc/sec)			
-74.0	5.9354	5.9799	6.0138	6.0495
-196.0	5.9802	6.0380	6.0807	6.1118

^aEstimated error: ± 0.0003 Mc/sec.

Table II. Observed chlorine frequencies in ThCl_4 .

Isotope	Frequency ^a (Mc)	Temperature (°C)
Cl^{35}	5.9193	25.3
Cl^{35}	5.9199	0.0
Cl^{35}	5.9202	-74.0
Cl^{35}	5.9181	-195.9
Cl^{37}	4.6645	-195.9

^aEstimated error: ± 0.0003 Mc.

Table III. Frequencies, in Mc/sec of resonances in NbCl_5^a

Transition	24.5°C		-195.7°C	
	Observed	Calculated	Observed	Calculated
Nb^{93} 1/2 - 3/2 ^b	5.4228 ₇	5.4228 ₆	5.7154 ₃	5.7154 ₂
Nb^{93} 3/2 - 5/2 ^b	6.0621 ₁	6.0618 ₅	6.0516 ₄	6.0513 ₃
Nb^{93} 5/2 - 7/2 ^b	9.5612 ₃	9.5612 ₇	9.5466 ₃	9.5466 ₃
Nb^{93} 7/2 - 9/2 ^b	12.9032 ₀	12.9033 ₀	12.9132 ₃	12.9133 ₉
Nb^{93} 1/2 - 5/2 ^c	11.486±0.002	11.4847		
Nb^{93} 1/2 - 7/2 ^c	21.046 ₇ ±0.001	21.0460		
Cl^{35} 1/2 - 3/2	13.0581 ₄ ^d		13.280 ^e	
Cl^{37} 1/2 - 3/2	10.2909 ^f		10.476 ^e	

^aParameters used in calculation of Nb frequencies are:

Parameter	24.5°C	-195.7°C
eqQ	78.080 ₉ ±0.002 Mc	78.260 ₄ ±0.002 Mc
η	0.32249±0.00002	0.34974±0.00002

^bEstimated accuracy of frequencies is ±0.0003 Mc/sec.

^cMeasured at 23.5°C with superregenerative circuit.

^dMeasured at 23.5°C.

^eMeasured at 196°C.

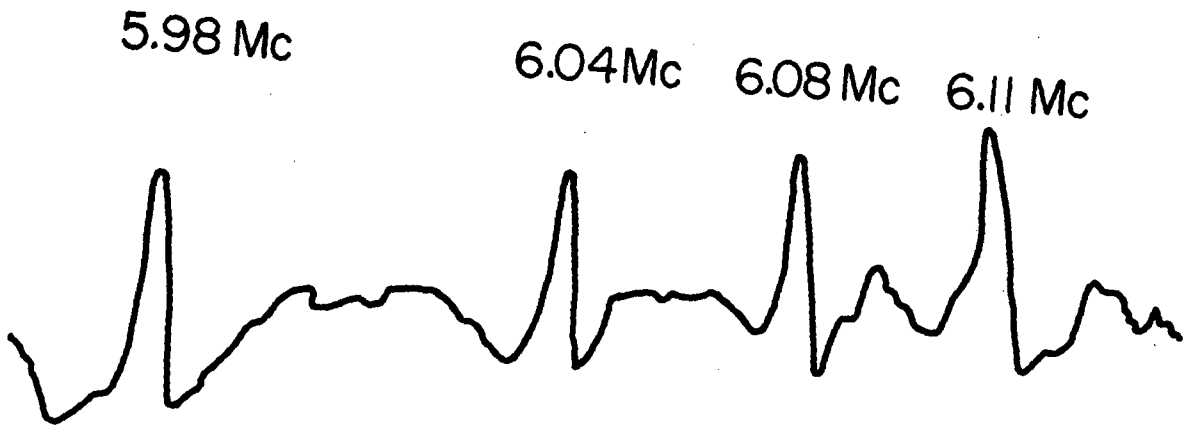
^fMeasured at 25.0°C.

LEGENDS

Fig. 1. Resonance of chlorine-35 in TiCl_4 at -196°C .

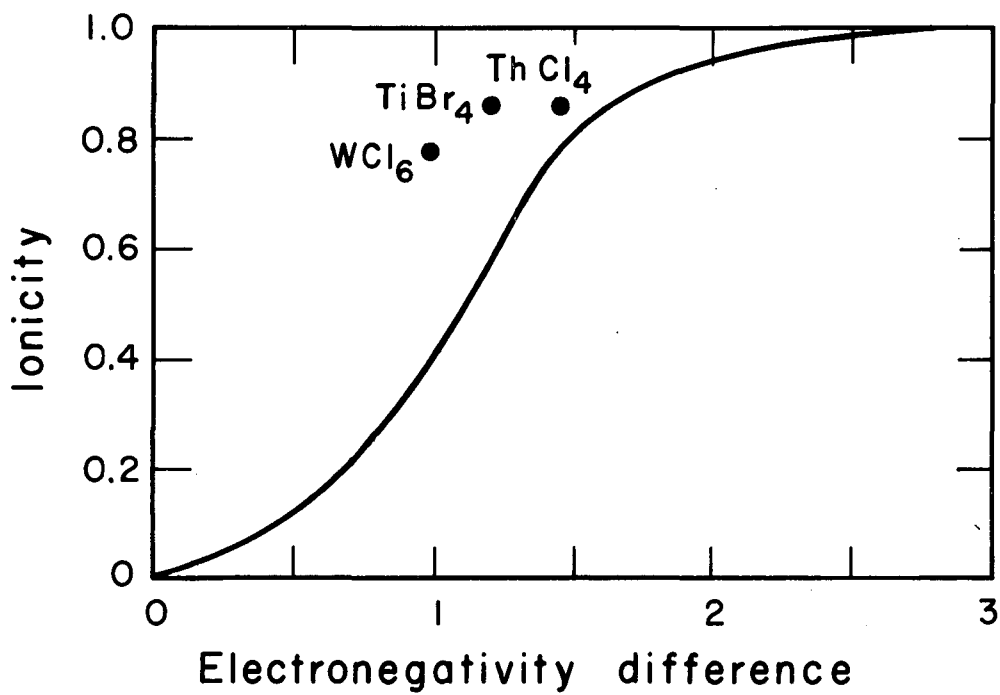
Fig. 2. Ionicities of halides from the relation $\beta = \nu / 0.85\nu_0$.

Fig. 3. Structure of NbCl_5 . Atomic radii are not to scale.



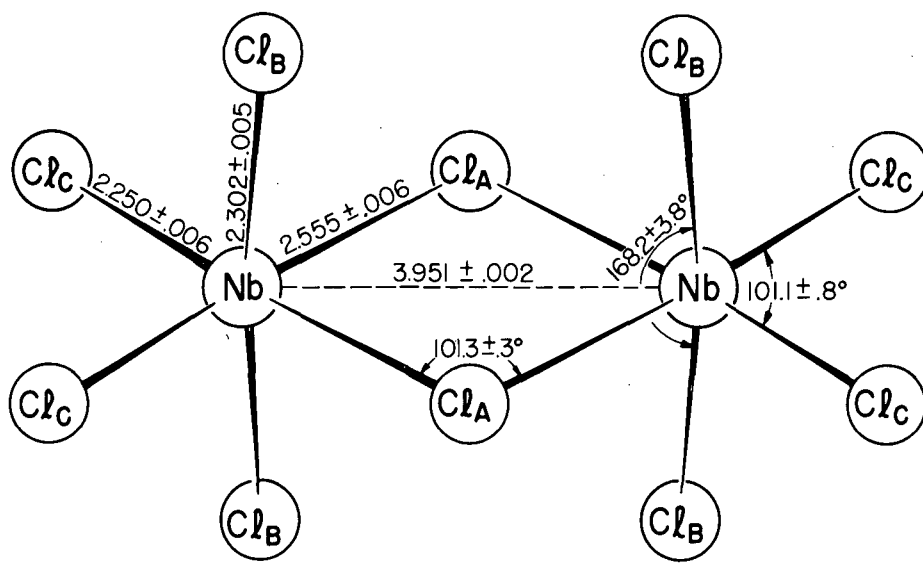
MU-19052

Fig. 1



MU - 22133

Fig. 2



NbCl_5

MU-19087

Fig. 3

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