

Taking the derivatives of (59) using (58) with (7) and (50) one gets

$$\chi_z = \sigma_z' / H_b \approx \sigma_0 / H_e,$$

$$C_{zzz} = \sigma_z'' / 6H_b^2 \approx -\sigma_0 H_d / 8H_e^3.$$

It can be easily verified that for both models, all the third-order coefficients apart from these calculated here,

are actually zero, as required by the symmetry of the crystal.

With the same technique one can also calculate the coefficients of the higher-power terms in the energy expansion. However, there is no point in doing this inasmuch as the experimental technique is not refined enough to measure these constants.

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Paramagnetic Resonance of Ni^{2+} and Ni^{3+} in TiO_2 †

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Electron spin resonance was observed in nickel-doped rutile. The majority of the nickel is in the divalent state, and probably occupies an interstitial position. The parameters describing the Ni^{2+} spectra are: $S=1$; $g[z]=2.20$; $g[y]=g[x]=2.10$; $D=-8.3 \text{ cm}^{-1}$; and $|E|=0.137 \text{ cm}^{-1}$ at 4.2°K . Some of the nickel, also probably occupying an interstitial position, is in the trivalent state, as was verified by oxidation-reduction tests. The parameters are: $S=\frac{1}{2}$ and $g[z]=2.254$; $g[c]=2.085$; $g[x]=2.084$. A third spectrum due to nickel in an unknown valence state appears after the sample is illuminated. It represents nickel in a substitutional site with $S=\frac{1}{2}$ and $g[110]=2.272$; $g[c]=2.237$; $g[1\bar{1}0]=2.050$.

I. INTRODUCTION

THE paramagnetic resonance of rutile, TiO_2 , containing 0.01% nickel grown at RCA Laboratories by M. Kestigian and E. Aleshin, was investigated.

Three distinctly different spectra were observed, which will be discussed separately. Afterwards data on the interrelationship and explanation of these spectra as also a comparison with copper- and cobalt-doped rutile will be given.

II. EXPERIMENTAL METHODS

A crystal of TiO_2 containing 0.01% nickel was used as its own dielectric cavity.¹ The rutile dielectric resonator has the advantage of possessing many resonances with large Q 's. The loaded Q 's (Q_L) were around 15 000 at 77°K and about 50 000 at 4.2°K .

The quality factor of the material (Q_M) can be obtained from measurements of the loaded cavity Q by using the relationship:

$$Q_{LR}^{-1} = Q_{L0}^{-1} + Q_M^{-1},$$

where Q_{LR} and Q_{L0} are the measured cavity Q 's on respectively, off paramagnetic resonance. The magnetic Q is a quality factor representing the absorption losses of the material and is defined by²:

$$Q_M = \frac{h\Delta\nu}{8\pi(n_2 - n_1)|\mu_{21}|^2 F},$$

where $\Delta\nu$ is the paramagnetic linewidth expressed in cycles per second; $(n_2 - n_1)$ is the population difference between the two levels per cc; $|\mu_{21}|$ is the matrix element for the transition and F is the filling factor which is unity for this cavity.

In principle, the concentration, which is simply related to the population difference $(n_2 - n_1)$, can be obtained from a measurement of the magnetic Q . The difficulty arises in trying to calculate the term $|\mu_{21}|$. $|\mu_{21}|$ depends on the orientation of the high-frequency magnetic field and therefore is dependent on the mode of the dielectric resonator which is unknown. Two approximate methods were used to obtain the concentration of the paramagnetic ions.

In one method, Q_M was measured for a large number of cavity resonances. The average of these values was then used in conjunction with the calculated space average value of $|\mu_{21}|$. In the second method, it was assumed that the smallest Q_M value corresponded to the largest value of $|\mu_{21}|$. This value of $|\mu_{21}|$ was computed and substituted in the formula for Q_M . From this the concentration was calculated. Both methods gave values for the concentration which agreed with each other within a factor of two.

In this manner it was found that the nickel-doped rutile crystal contained about eighty parts per million Ni^{2+} , five parts per million Ni^{3+} and two parts per million of a light-generated nickel center.

The microwave spectrometer that was used consisted of a stabilized source and a superheterodyne detection scheme with scope presentation.

The crystal was oriented with x-ray analysis by G. W. Neighbor of RCA Laboratories. The crystallographic axes were independently checked by observing

† Partially supported by the U. S. Army Signal Corps.

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¹ (a) H. J. Gerritsen and H. R. Lewis, *Quantum Electronics* (Columbia Press, New York, 1960), p. 385. (b) A. Okaya, *Proc. IRE* 48, 1921 (1960).

² T. H. Maiman, *Quantum Electronics* (Columbia Press, New York, 1960), p. 324.

TABLE I. Angles between magnetic axes and crystallographic directions for Ni^{2+} ion.

Magnetic axes	Ion	[001]	[110]	[110]
X	1 and 3	90°	$\pm 84.6^\circ$	$\mp 5.4^\circ$
X	2 and 4	90°	$\mp 5.4^\circ$	$\pm 84.5^\circ$
Y	1,2,3,4	0°	90°	90°
Z	1 and 3	90°	$\mp 5.4^\circ$	$\pm 84.6^\circ$
Z	2 and 4	90°	$\pm 84.6^\circ$	$\mp 5.4^\circ$

the paramagnetic resonances of the iron and chromium impurities which were present in a concentration of about 5 parts per million.

III. DIVALENT NICKEL

As estimated 90% of all nickel present is divalent. This ion gives rise to broad resonance lines, which are observable at a temperature of 77°K and below. In the crystal studied these lines had a width varying from 80 gauss to over 800 gauss. Converted into frequency, these widths were all 150 Mc/sec within 25%.

The resonance diagrams observed at 4.2°K for 9.3 kMc/sec and 18.06 kMc/sec are shown in Figs. 1-3 for the (110) and (001) planes. It follows from these figures that there are four ions in the unit cell, of which the orientation of the magnetic axes are shown in Table I.

The angle in the (001) plane which the magnetic axes of the ions make with the [110] and [110] crystallographic directions was measured at both 77° and 4.2°K to be $5.4^\circ \pm 0.2^\circ$. This angle is hereafter denoted as α . In Sec. VII the problem of the four ions in the unit cell is further discussed.

In Fig. 4 a plot is made of the resonance fields along the magnetic axes for a range of frequencies around 8.25 kMc/sec. From the nature of this plot which shows a zero-field splitting of 8.25 kMc/sec, the spin was established to be either one or two. Divalent nickel would have a spin of one, while tetravalent nickel, having six d electrons, would probably be diamagnetic

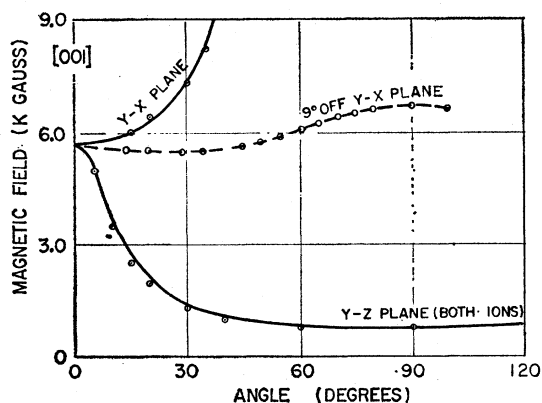


FIG. 1. The points are the resonances of Ni^{2+} in TiO_2 at 4.2°K, 9334 Mc/sec and in a plane close to (110). The solid lines represent the theoretical resonance fields.

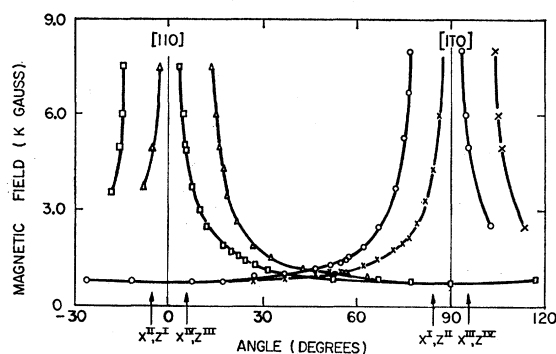


FIG. 2. The points are the resonances of Ni^{2+} in TiO_2 in the (001) plane at 4.2°K and 9238 Mc/sec. The solid lines represent the theoretical resonance fields.

with $S=0$, but a spin value of two or perhaps one might exist if the crystal field were sufficiently weak.

Apart from the fact that tetravalent nickel would require an enormous amount of ionization energy and thus would probably not be stable, an experiment on reduced nickel-doped rutile decided unambiguously that the valence state was divalent. This experiment will be described in Sec. VI.

The usual Hamiltonian for an $S=1$ ion in orthorhombic surroundings is³

$$H_{op} = \beta(\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}) + D(S_z^2 - \frac{2}{3}) + E(S_x^2 - S_y^2). \quad (1)$$

The energies of the three levels in zero magnetic field are: $\frac{1}{3}D - E$, $\frac{1}{3}D + E$, and $-\frac{2}{3}D$. Along the magnetic axes the resonance conditions are:

$$z \text{ axis: } h\nu = 2(E^2 + g_z^2\beta^2H^2)^{\frac{1}{2}},$$

$$c \equiv y \text{ axis: } h\nu = \frac{1}{2}D + \frac{3}{2}E + [\frac{1}{4}(D-E)^2 + g_y^2\beta^2H^2]^{\frac{1}{2}},$$

$$x \text{ axis: } h\nu = \frac{1}{2}D - \frac{3}{2}E + [\frac{1}{4}(D+E)^2 + g_x^2\beta^2H^2]^{\frac{1}{2}}.$$

The only transitions observed in the experiments were between those levels which go to the 8.25-kMc/sec zero-field splitting. Intensity measurements at 4.2° and 1.3°K showed that these levels have the lowest energy, so that D is negative.

The parameters which give a good fit with experimental data are:

$$g_x = 2.10 \pm 0.05; \quad g_y = 2.10 \pm 0.05; \quad g_z = 2.20 \pm 0.05, \quad (2)$$

$$|E| = 4.125 \pm 0.02 \text{ kMc/sec},$$

$$D = -250 \pm 5 \text{ kMc/sec}.$$

The solid lines in Figs. 1-4 were obtained by programming a computer to obtain solutions of Eq. (1) for the xy , xz , and yz planes, using the parameters given in (2). A theoretical plot of the energy levels as a function of the magnetic field along the three principal axes is given in Fig. 5.

The experiments in the (001) plane could thus be

³ K. D. Bowers and J. Owen, *Reports on Progressive Physics* (The Physical Society, London, 1955), Vol. 18, p. 348.

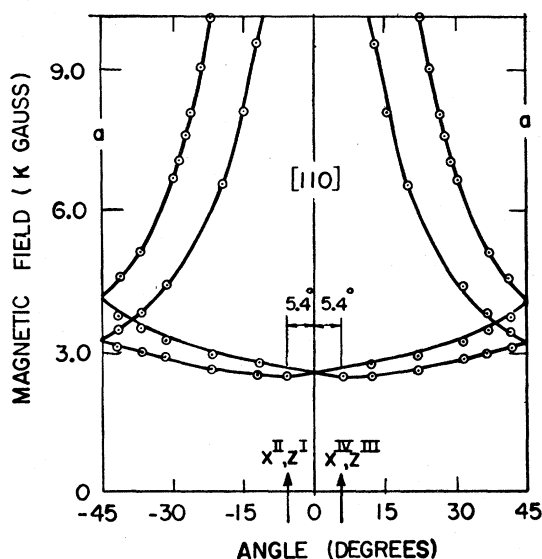


FIG. 3. The points are the resonances of Ni^{2+} in TiO_2 in the (001) plane at 4.2°K and 18.06 kMc/sec. The solid lines represent the theoretical resonance fields.

compared immediately with the computations, since the (001) plane is the xz plane. The magnetic x and z axes are indicated in Fig. 2. Since the magnetic axes are $\pm 5.4^\circ$ away from the $[110]$ direction, the (110) plane does not exactly coincide with the yx and yz planes. This is important since the resonances in the yx plane are very sensitive to orientation. In Fig. 1 the plane in which the magnetic field was rotated was 3.5° away from the (110) plane in such a way that the yx plane of one ion was misoriented by 2° and of the other ion by 9° .

The two differently oriented ions in the yz planes still have resonances that coincide within the linewidth. For the two ions in the yx planes there is a wide separation between the resonances so that for 90° one resonance is observed in the yx plane at 6.7 kgauss. From Fig. 2 one sees that this corresponds to an angle between magnetic field and x axis of 9° for the one ion. The theoretical curve fits the data for the ion whose x axis is 2° off quite well.

IV. TRIVALENT NICKEL SPECTRUM

When nickel-doped rutile was first studied, the most clearly observable spectrum was that due to trivalent nickel.⁴ To our surprise resonance lines of a width of only two gauss were observed at room temperature with $S = \frac{1}{2}$ and a rather isotropic g value slightly in excess of two. It was learned in subsequent experiments that this spectrum was caused by only 7% of the nickel present. This number is reliable within a factor of about two.

Ni^{3+} is isoelectronic with Co^{2+} , having seven d electrons. Co^{2+} salts in crystal fields of the kind that exist in rutile show resonance lines which are very wide at

room temperature, and are only sharp enough to be observed at 78°K or sometimes 20°K. The g value is very anisotropic and varies from three to six in a typical case.⁵

The behavior of Ni^{3+} is thus entirely different from that of Co^{2+} . D. S. McClure of RCA Laboratories suggested that the crystal field in the case of Ni^{3+} is sufficiently large to cause spin quenching. Co^{2+} in the kind of crystal referred to earlier⁵ has seven d electrons which are distributed according to $e^5\gamma^2$, while the stronger crystal field in Ni^{3+} causes the lower lying e levels to be filled completely, resulting in the configuration $e^6\gamma^1$. This configuration explains the observed behavior of Ni^{3+} . Covalent bonding would, of course, have the same effect and which of the two descriptions is more appropriate is unknown.

The resonance diagrams of the Ni^{3+} ion are shown in Figs. 6 and 7. Similar to that of Ni^{2+} , Ni^{3+} has four ions in the unit cell. The g values were measured at 9.264 kMc/sec and 25.110 kMc/sec and do not vary from room temperature down to 4.2°K. They are:

$$g(c) = 2.085; \quad g(x) = 2.084; \quad g(z) = 2.254 \pm 0.003.$$

The magnetic y axes of the four ions coincide along the c axis. The x and z axes are situated in the (001) plane, making an angle α of $\pm(9.1^\circ \pm 0.3^\circ)$ with the $[110]$ and $[\bar{1}\bar{1}0]$ directions. This angle is the same within the experimental accuracy at 292°, 77°, and 4.2°K. The linewidths of the resonances are two gauss at 292°K and 1.2 gauss at 78° and 4.2°K.

V. LIGHT-GENERATED NICKEL

If the crystal is illuminated at room temperature and immediately cooled, another narrow-line spectrum in addition to the Ni^{2+} spectrum is observed. This spectrum will be referred to as the spectrum of the "light-generated nickel." With sufficient illumination, this spectrum can be made to have an intensity comparable to that of the Ni^{3+} .

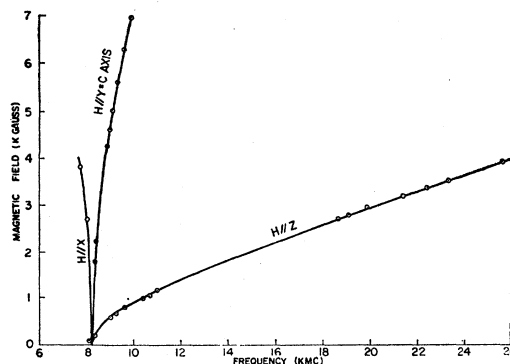


FIG. 4. Resonance frequency vs magnetic field along the three magnetic axes of Ni^{2+} in TiO_2 . The solid lines represent the theoretical resonance fields.

⁴ H. J. Gerritsen and E. S. Sabisky, Bull. Amer. Phys. Soc. **3**, 235 (1961).

⁵ B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. **A205**, 336 (1951).

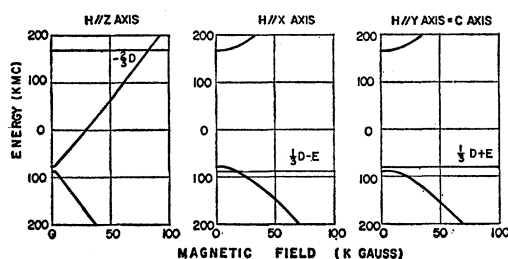


FIG. 5. Theoretical curves of Ni^{2+} in TiO_2 for a magnetic field along the three magnetic axes.

The ratio of the intensities of the light-generated nickel and the Ni^{3+} , measured with the magnetic field along the c axis, increases with increasing illumination up to a certain limit, above which it becomes constant. This constant value can easily be reached with exposure by an ordinary microscope lamp, 10 cm from the sample, for a few minutes. The effect was the same without a filter or for a filter that cuts off at wavelengths shorter than 5000 Å. This means that band gap radiation does not cause this phenomenon, but rather light of much longer wavelength. (The bandgap of rutile is in the near uv.) Subsequent uv irradiation did not change the ratio substantially. The exact ratio of the intensities of the light-generated nickel to the Ni^{3+} depends sensitively on the oxidation state of the crystal. The crystals are grown in a hydrogen flame and thus are strongly reduced when obtained. If the crystal is heated for ten hours at 800°C in one atm of oxygen, the maximum ratio of the light-generated spectra to the Ni^{3+} spectrum is $\frac{1}{5}$. This ratio was found to increase to $\frac{1}{3}$ after the crystal was heated for 24 hr at 800°C in one atm of oxygen.

The resonance diagrams, Figs. 6 and 7, show that the light-generated center has the same symmetry characteristics as the Ti^{4+} site and most probably is substitutional nickel. The g values were measured at 78° and 4.2°K at X - and K -band frequencies. They are:

$$g(c) = 2.237; \quad g[110] = 2.050; \quad g[1\bar{1}0] = 2.272 \pm 0.003.$$

The magnetic axes coincide within 0.2° (the experimental accuracy) with the c , $[110]$, and $[1\bar{1}0]$ directions as obtained from the chromium and iron impurities also present in the crystal.

The linewidth of the light-generated nickel at 78° and 4.2°K is 0.9 gauss or 2 Mc/sec. Above 200°K the linewidth increases rapidly which is probably due to spin-lattice interaction and at room temperature a broad line is visible after illumination. The light-generated spectrum disappears when the sample is kept at room temperature in the dark for a day.

There was no difference in the strength of the resonances when the sample was either illuminated at room temperature and then cooled to 77° or when the sample was illuminated while at 77°K. When the sample was illuminated at 4.2°K, two additional resonances, a few

times weaker than the light-generated resonances were observed. These were not analyzed.

We have been able to observe the growth of the light-generated nickel resonance during illumination but were unable to detect a decrease in intensity of either the Ni^{2+} or the Ni^{3+} resonance. We believe that our sensitivity and reproducibility would have allowed us to see such an effect for Ni^{3+} but not for Ni^{2+} if it were present. The conclusion is thus that the light-generated nickel probably does not grow at the expense of Ni^{3+} , under illumination, but is independent of it.

There is uncertainty as to whether the light-generated nickel represents trivalent nickel or monovalent nickel.

Monovalent nickel has been observed in nickel-doped magnesium oxide after ultra violet irradiation⁶ and also in nickel-doped sodium fluoride after irradiation.⁷ It was hoped that study of the hyperfine structure constant due to the Ni^{61} isotope might solve the question of the valence state. The presence of other impurities prevented observation of the hyperfine lines, which are expected to have an intensity of 0.3% of the main nickel resonance. A future experiment with nickel-doped rutile, enriched with Ni^{61} is planned.

VI. REDUCTION OXIDATION EXPERIMENTS

Before the reduction experiment was done, three possible choices were open as to the valence state of the two spectra observed in unilluminated nickel-doped rutile. These were:

1. Broad spectrum is Ni^{4+} , narrow spectrum is Ni^{3+} or Ni^{2+} ;
2. Broad spectrum is Ni^{2+} , narrow spectrum is Ni^{2+} ;
3. Broad spectrum is Ni^{2+} , narrow spectrum is Ni^{3+} .

The last possibility seems the most reasonable one and

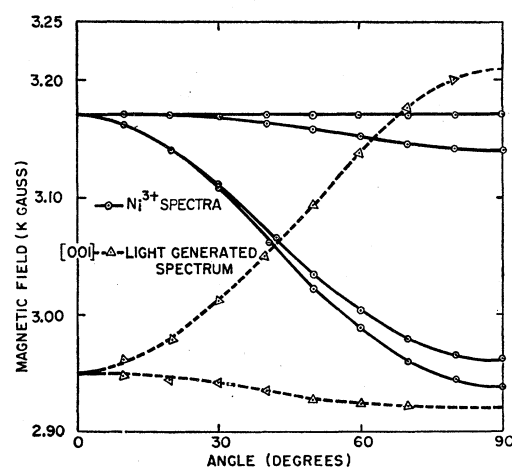


FIG. 6. Narrow line spectra of nickel-doped rutile close to the (110) plane at 77°K and 9264 Mc/sec.

⁶ J. W. Orton, P. Auzins, J. H. E. Griffiths and J. E. Wertz (to be published).

⁷ W. Hayes and D. A. Jones, Proc. Phys. Soc. **71**, 503 (1958).

indeed the one found to be in agreement with the reduction experiment. One expects in the case of reduction, that the ions will favor the lowest valence state. Since it was observed that the strength of the broad line spectrum was unchanged upon reduction, whereas the narrow line spectrum disappeared almost completely, only the third possibility could have been realized. No light effect was observed in the reduced sample. It was also observed that reduction increases the intensity of the impurity chromium spectrum, which is probably due to the conversion of tetravalent into trivalent chromium. Reduction decreased the intensity of the iron spectrum, due to conversion of trivalent iron into divalent iron.

In the reduced sample a new center with lines a few gauss in width was observed along the $[110]$ direction. The magnetic field of the resonances was measured at a few frequencies from which a g value of about ten was derived. These lines were also observed in the reoxidized sample, but with decreased intensity corresponding to a concentration of about 0.2 part per million. Away from the $[110]$ direction the g value decreased. Since these lines were not observed in undoped reduced rutile, the lines are probably due to nickel. A speculation is that the vacuum heating reduced part of the Ni^{3+} to Ni^{2+} while the rest of the Ni^{3+} lost one or more of the neighboring O^{2-} atoms. The resulting crystalline electric field might now not be strong enough for spin quenching to take place and the resulting center would behave as divalent cobalt, having the $e^5\gamma^2$ configuration. Another possibility is that hydrogen, which is present in the lattice, plays a role.

The crystal was reduced by heating it for twenty minutes at 700°C in vacuum.

VII. SUBSTITUTIONAL AND INTERSTITIAL SITES IN RUTILE

Since the light-generated nickel has the symmetry of a Ti^{4+} site, the simplest explanation is that this nickel ion replaces Ti^{4+} in the lattice. This type of symmetry

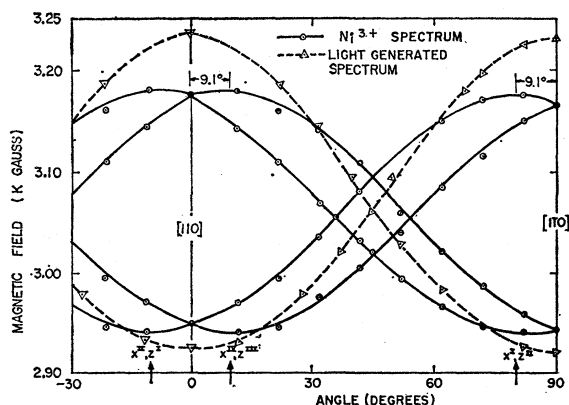


FIG. 7. Narrow line spectra of nickel-doped rutile in (001) plane at 77°K and 9242 Mc/sec .

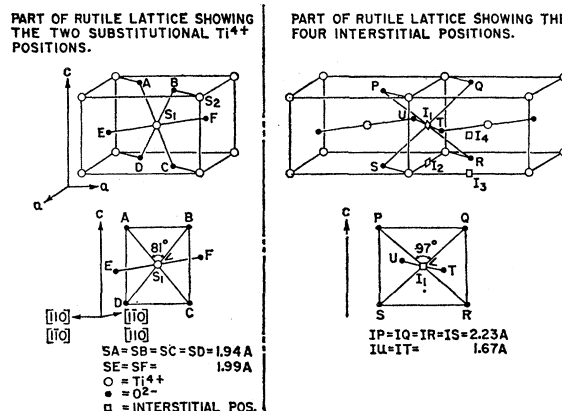


FIG. 8. Substitutional and interstitial lattice positions in TiO_2 .

has also been observed in TiO_2 doped with Cr^{3+} ,⁸ Fe^{3+} ,⁹ V^{4+} ,¹⁰ and Mn^{4+} .¹¹ If this explanation is correct, it implies that the parent center, Ni^{2+} or Ni^{4+} , from which the light-generated nickel is created by electronic excitation under illumination, is situated in a substitutional site.

P. F. Chester¹² observed a spectrum due to four ions in the unit cell, namely in TiO_2 with Ti^{3+} . He originally explained this spectrum by assuming that the Ti^{3+} was located at a Ti^{4+} site but with O^{2-} vacancies in the next nearest neighbor position in the (001) plane.

He rejected this idea in a subsequent study since the position assigned to the O^{2-} vacancies that are associated with the Ti^{3+} ions seems artificial.

Another difficulty is that one O^{2-} vacancy should create two Ti^{3+} ions because of charge compensation. This would give rise to two spectra of equal intensity, one due to substitutional Ti^{3+} and one due to Ti^{3+} with O^{2-} vacancy, unless one assumes in addition that both Ti^{3+} ions share one O^{2-} vacancy, which seems unlikely.

The simplest explanation is that the Ti^{3+} occupies an interstitial lattice position. This explanation is believed to be equally valid for the Ni^{2+} and Ni^{3+} ions.

Figure 8 represents a sketch of the substitutional and interstitial sites in rutile. A separate sketch shows the six nearest-oxygen ions surrounding the centers. For both centers the arrangement is so that four oxygens are situated at the corners of a rectangle, while the line connecting the center with the other two ions is perpendicular to that plane. The distances between the center and the oxygen ions are calculated from the unit

⁸ (a) H. J. Gerritsen, S. E. Harrison, H. R. Lewis and J. P. Wittke, *Phys. Rev. Letters* **2**, 153 (1959). (b) E. Sierro, K. A. Muller, R. Lacroix, *Arch. Sci. (Geneva)* **12**, 122 (1959).

⁹ A. Okaya, D. Carter and F. Nash, *Bull. Amer. Phys. Soc.* **3**, 73 (1960).

¹⁰ (a) H. J. Gerritsen and H. R. Lewis, *Phys. Rev.* **119**, 1010 (1960). (b) G. M. Zverev and A. M. Prokhorov, *JETP* **39**, 222 (1960).

¹¹ H. G. Andresen, *Phys. Rev.* **120**, 1606 (1960).

¹² P. F. Chester, *Proceedings of the Conference on Semiconductor Compounds*, New York, 1961 (to be published).

cell dimensions as given in Grant's review article on TiO_2 .¹³

In the substitutional position, the six O^{2-} ions are all at about the same distance from the Ti^{4+} . If one takes 1.26 Å for the radius of O^{2-} , an ion with radius larger than 0.68 Å has to push the four oxygens in the plane apart. When the radius is larger than 0.73 Å, the ion has also to push the O^{2-} ions *E* and *F* apart.

In the interstitial position, an ion with radius larger than 0.41 Å has to push the O^{2-} ions *U* and *T* apart but only when the radius is large than 0.97 Å does the ion also have to push the four oxygens in the plane apart.

This information makes it plausible that ions with radii smaller than 0.73 Å prefer a substitutional position. The radii of the substitutional ions: Ti^{4+} , Cr^{3+} , Fe^{3+} , V^{4+} , and Mn^{4+} are indeed all between 0.61 and 0.68 Å. The radius of Ti^{3+} is 0.76 Å and of Ni^{2+} 0.78 Å, and these ions go in the interstitial lattice positions. The radius of Ni^{3+} is not known but probably close to 0.65 Å, which suggests that it would go in the substitutional site, rather than the experimentally observed interstitial position. A possible explanation is that under the reducing conditions existing during crystal growth, almost all the nickel is interstitial Ni^{2+} . Subsequent partial oxidation may oxidize some Ni^{2+} to Ni^{3+} , without affecting its position in the lattice.

There are two substitutional sites in the unit cell namely at (0,0,0) and $(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}c)$. For the one center the *EF* direction is along $[110]$, for the other center the *EF* direction is along $[1\bar{1}0]$.

There are four interstitial sites in the unit cell namely at $(0, \frac{1}{2}a, 0)$, $(\frac{1}{2}a, 0, 0)$, $(0, \frac{1}{2}a, \frac{1}{2}c)$, and $(\frac{1}{2}a, 0, \frac{1}{2}c)$. They all have the same local surroundings, but the *UT* directions make angles of $\pm 12.5^\circ$ and $\pm 77.5^\circ$ with the $[110]$ direction.

Since large interstitial ions have to move the two O^{2-} ions *U* and *T* outwards, it is likely that distortion sets in, which would change the angle α from the unperturbed value of 12.5° . If one assumes this, then the explanation of the Ti^{3+} , Ni^{2+} , and Ni^{3+} spectra as due to an interstitial position is in agreement with the experiments. It is interesting to note that the α value of 9.1° for the small Ni^{3+} ion is closest to the unperturbed value of 12.5° , while the large ions Ni^{2+} with $\alpha = 5.4^\circ$ and Ti^{3+} with $\alpha = 19^\circ$ deviate rather strongly thereof.

A third possible explanation of the observed 4 ion spectra should be mentioned. The high dielectric constant of rutile indicates that the structure is on the verge of ferroelectricity. It seems possible that some substitutional ions may induce this ferroelectric behavior locally, in which case the ion would move off center possibly in such a way as to give rise to 4 centers rather than the 2 substitutional centers. A strong argument against this explanation is that in the case of Ni^{3+} the value of the angle α varies less than 2% between 298° and 4.2°K but the dielectric constant varies by a

factor of 1.6. For the Ni^{2+} ion the variation of α was less than 2% over a temperature range where the dielectric constant changes by 10%.

It is not presently known how charge compensation is maintained when ions are introduced interstitially. Principally this can be effected by either omission of some Ti^{4+} ions from the lattice or by introducing interstitial O^{2-} . It is even conceivable that hydrogen, which is always present in these crystals¹⁴ could compensate the excess positive charge when some Ti^{4+} ions are replaced by H^+ ions.

VIII. COMPARISON OF THE SPECTRA OF RUTILE DOPED WITH NICKEL, COPPER, AND COBALT

In nickel-doped rutile, the spectra due to the d^8 and d^7 electrons have been established. It is interesting to compare these spectra with spectra due to copper- and cobalt-doped rutile.

Copper-doped rutile shows a spectrum which is attributed to divalent copper, which has 9 *d* electrons. Ni^{2+} also has 9 *d* electrons and may possibly be the valence state of the light-generated spectra. The copper spectrum is complicated due to the two nuclear isotopes which each have a spin of $\frac{3}{2}$ and to quadrupole lines. Moreover, the extremely long spin-lattice relaxation time of ten seconds at 4.2°K , measured in a crystal containing 30 parts per million of copper, makes observation difficult. From the preliminary data, the spectrum appears to be a substitutional (two-ion) spectrum. The radius of Cu^{2+} (0.72 Å) suggest that the interstitial site might be favored.

The following preliminary data have been obtained:

$$\begin{array}{ll} g_e = 2.093, & A_e = -0.0029 \text{ cm}^{-1}, \\ g_{110} = 2.105, & A_{110} = -0.0019 \text{ cm}^{-1}, \\ g_{1\bar{1}0} = 2.344, & A_{1\bar{1}0} = -0.0088 \text{ cm}^{-1}. \end{array}$$

These values compare well with those of Cu^{2+} in Tutton salt, where *g* values of 2.4 and 2.13 are obtained with *A* values of -0.010 cm^{-1} and 0.0034 cm^{-1} .¹⁵

The *g* values are very different from those observed for the light-generated nickel which supports the idea that light-generated nickel is not Ni^{2+} but Ni^{3+} .

Cobalt-doped rutile gave negative results. Although a large quantity, 100 parts per million, of cobalt was present in the crystals giving them a greenish color, it must all have been present as trivalent cobalt, which is probably diamagnetic with 6 *d* electrons filling the lower triplet. No paramagnetic resonance was observed. Irradiation with 100 mr of γ rays did not succeed in converting even a few percent of the trivalent cobalt to divalent cobalt which would have been observed in paramagnetic resonance.

¹⁴ (a) D. C. Cronmeyer, Phys. Rev. **113**, 1222 (1959). (b) B. H. Soffer, Massachusetts Institute of Technology Laboratory for Insulation Research, Technical Report 140, 1959 (unpublished).

¹⁵ B. Bleaney, K. D. Bowers and D. J. E. Ingram, Proc. Roy. Soc. (London) **A228**, 147 (1955).

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TABLE II. Parameters of $\text{TiO}_2\text{:Ni}$ at 4.2°K.

Ion	Concent. by weight	No. ions in unit cell	Spin	g values			Zero-field splitting (kMc/sec)	Linewidth (Mc/sec)	Angle α (degree)
				g_e	g_x	g_z			
Ni^{2+}	80×10^{-6}	4	1	2.10	2.10	2.20	8.2 ⁵ and 250	150	5.4
Ni^{3+}	5×10^{-6}	4	$\frac{1}{2}$	2.085	2.084	2.254	...	2	9.1
Light-gen. Ni	2×10^{-6}	2	$\frac{1}{2}$	2.237	2.272	2.050	...	2	0

IX. COMMENTS ON THE USE OF DIVALENT NICKEL IN RUTILE FOR HIGH-FREQUENCY MASER APPLICATION

The large zero-field splitting of $\text{TiO}_2\text{:Ni}^{2+}$ make it attractive for maser purposes. Continuous wave saturation measurements indicated that at 4.2°K the spin-lattice relaxation time of all three nickel ions is of the order of 50 msec. The deciding factor as to the usefulness of divalent nickel in rutile for maser applications is the linewidth. The linewidth of Ni^{2+} in the crystals used for these experiments was 150 Mc/sec. However, for maser applications, the concentration of nickel must be increased by a factor of about five. These heavier concentrations may cause excessive strains in the lattice and thereby widen the lines appreciably above the value of 150 Mc/sec.

If the lines are still reasonably narrow in a more heavily doped sample, an experiment may be performed with a crystal doped with both iron and nickel. The iron resonance line may be saturated at a frequency of about 125 kMc/sec; then by the process of second harmonic coupling and cross relaxation, the nickel resonance at

250 kMc/sec may also become saturated. Another transition in the iron could conceivably be used for idler doping. In that case the region from 200–300 kMc/sec would be open for maser amplification techniques.

X. CONCLUSIONS

The data on nickel-doped rutile are summarized in Table II.

The first two spectra are interpreted as interstitial nickel, the last one as substitutional nickel.

The long relaxation time seems to make Ni^{2+} a useful ion for maser application if the linewidth in more concentrated crystals does not widen excessively.

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