

radical. Further it has been shown¹⁶ that the catalytic sites can be inactivated by chemisorption compounds such as quinoline. The decrease in catalytic activity is linearly related to the amount of nitrogen compound chemisorbed.

In our experiments we adsorbed quinoline on the activated zeolite and intense e.s.r. signals were obtained. Here again a charge-transfer complex simi-

lar to that formed by $(C_6H_5)_3N$ is formed in the crystal lattice. At present, it appears that the $(AlO_{3/2})$ electron traps in the crystal lattice are responsible, first for the strong adsorption of organic molecules with low ionization potential which form charge-transfer complexes and, secondly, for the catalytic activity of these types of crystals in heterogeneous catalytic hydrocarbon reactions.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Paramagnetic Resonance Absorption of γ -Irradiated Synthetic Zeolites

BY DENNIS N. STAMIREN AND JOHN TURKEVICH

RECEIVED SEPTEMBER 3, 1963

A study has been carried out on the effect of γ -irradiation of synthetic zeolites. Sodium X and sodium Y zeolites and also decationated samples prepared from these were irradiated under vacuum at room temperature with doses up to 20 megaroentgens. Two types of e.p.r. signals were obtained. For the sodium Y and the sodium X zeolite a single line signal X_1 was found. It was 38.4 gauss wide with $g = 2.0200$, indicating that it is a hole; its intensity followed the Curie law. Heating above 350° caused the signal to disappear. The signal was decreased by oxygen gas, but the effect was reversible. Saturation does not take place with irradiation up to 14 megaroentgens. A pink coloration was also produced, but its behavior did not parallel that of the X_1 signal. For the decationated Y zeolite a six-lined e.p.r. signal was obtained by radiation. The separation between the lines was 5 gauss and the center of this signal was at $g = 2.0017$. Its intensity was independent of temperature and the signal annealed at about 500° . The signal is not affected by oxygen and its intensity saturates at an exposure of 3 megaroentgens; no coloration was observed. For partially decationated sites both X_1 and X_2 signals were observed. The X_1 signal is interpreted to be a hole located on the oxygen of the lattice while the X_2 is assumed to be due to an electron located near the Al^{27} nucleus that has been decationated.

Introduction

The nature of the various types of defects in solids produced by high energy irradiation has been successfully studied in many cases by the method of paramagnetic resonance.¹⁻³ These defects usually give rise to characteristic absorption spectra which have been used to study such defects. However, most of the defects are paramagnetic centers, and e.s.r. measurements provide very useful information about the type of defect, its environment, and crystal field symmetry. The host lattice plays an important role in formation and identification of the defects. First, non-paramagnetic structural changes in the lattice can modify the field symmetry near the paramagnetic center which, in turn, alters the e.s.r. spectrum.^{4,5} Secondly, by incorporation (or present as an impurity) of atoms with magnetic nuclei in the lattice, nearby holes or electrons can be identified through hyperfine structures found in the e.s.r. spectra. Such is the case in the magnetic resonance of irradiated quartz,^{2,3} where the paramagnetic hole is located near an aluminum atom (present as an impurity) which gives rise to a six-line hyperfine structure. We irradiated polycrystalline aluminosilicates, namely synthetic zeolites, with γ -rays where the quantity, position, and state of the aluminum in the aluminosilicate framework was known. By suitably modifying the coordination of the aluminum $[AlO_{4/2}^-]$ with the oxygens of the lattice, a hole can be produced at the $[AlO_{3/2}]$ unit which can trap an electron. This exhibits a characteristic e.s.r. with a hyperfine structure. On the other hand, when the aluminum is present in the original four-coordinated state which is isomorphous with the silicon present

($SiO_{4/2}$), a paramagnetic hole, but not an electron, is observed. This hole has no hyperfine structure and exhibits different magnetic constants. The ratio of alumina units possessing vacancies to those with none can be varied, which in turn determines the individual relative intensities of the resonances of the hole and electron which are observed simultaneously in the e.s.r. spectrum. The electrons produced by irradiation can be observed only if trapped by the vacancies; otherwise only the holes are observed.

Experimental

A. Sample Preparation.—The Linde type X and Y synthetic crystalline zeolites were used, having the compositions $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$ and $Na_{88}[(AlO_2)_{88}(SiO_2)_{104}]$ of the unit cell, respectively.

The ammonium exchange samples were prepared by contacting the Na zeolite with an aqueous NH_4NO_3 solution, using the conventional ion-exchange technique. All the samples used for irradiation were degassed at 500° under vacuum ($\sim 10^{-3}$) in a system free of stopcock grease. This thermal activation was carried out for at least 15 hr. The samples were then sealed under vacuum in quartz tubes (of 5 mm. o.d.). The samples in the quartz tubes were irradiated with a Co^{60} γ -source of about 4000 curies intensity. In all cases, except otherwise stated, a dose rate of approximately 1.9×10^7 roentgens was used. All samples were irradiated at room temperature. Before the e.s.r. measurements were performed, the powdered samples (about 1 in. length in the 5-mm. quartz tube) were kept in one end of the tube while immersed in an ice-water bath, while the other end was heated to 600° to obtain complete annealing. This treatment completely eliminates the e.s.r. found in the irradiated quartz tube. Then the powder was transferred to the annealed part of the tube and the e.s.r. spectra were obtained. This procedure proved to be more convenient than transferring the irradiated powders in a drybox from irradiated to nonirradiated tubes.

B. E.s.r. Measurements.—A Varian spectrometer (Model V4500) operating at 9.5 kMc./sec. and at TE_{102} mode was employed. The magnetic field was modulated at 100 kc./sec. and was measured by a proton magnetic resonance gauss meter. Varian conventional low temperature equipment was used. Low microwave powers were obtained with the Varian matching low power cavity. Spin concentrations were obtained by using a single crystal of $CuSO_4 \cdot 5H_2O$ with known susceptibility as a standard.

Results and Discussion

A. E.s.r. Absorption in the Irradiated NaX and NaY Zeolites.—A single e.s.r. line in both types of zeo-

(1) T. H. E. Griffiths, T. Owen, and I. M. Ward, "Defects in Crystalline Solids," Physical Society Report of Bristol Conference, London, 1954.

(2) M. O. M. O'Brien and M. H. L. Pryce, "Defects in Crystalline Solids," Physical Society Report of Bristol Conference, London, 1954.

(3) D. S. Billington and J. H. Crawford, "Radiation Damage in Solids," Princeton University Press, Princeton, N. J., 1961.

(4) T. E. W. Wertz, T. Worton, and P. Auzins, *Discussions Faraday Soc.*, **31**, 140 (1961).

(5) M. H. Cohen, W. Kanzig, and T. O. Woodruff, *Phys. Rev.*, **108**, 1096 (1957).

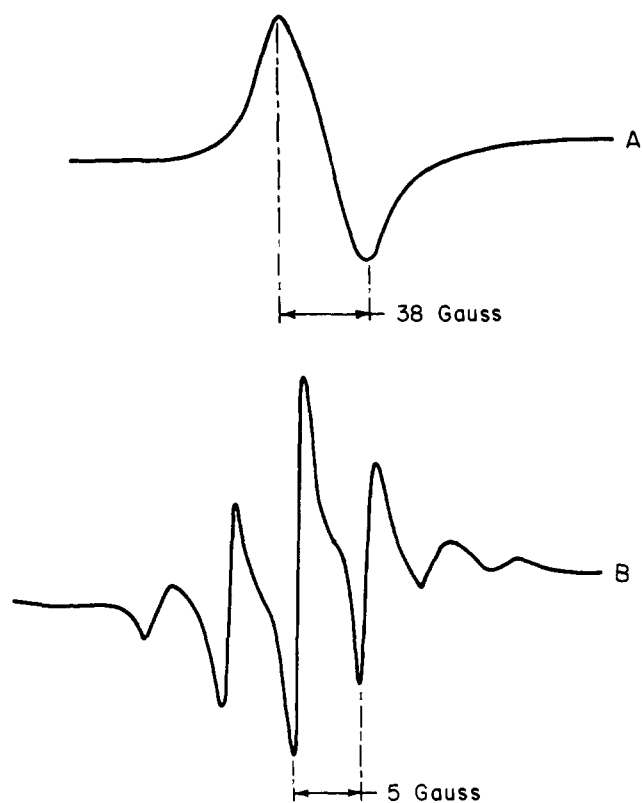


Fig. 1.—E.s.r. adsorption of γ -irradiated NaY zeolite, $g = 2.0200$ (A); e.s.r. adsorption of γ -irradiated decationized Y zeolite, $g = 2.0017$ (B).

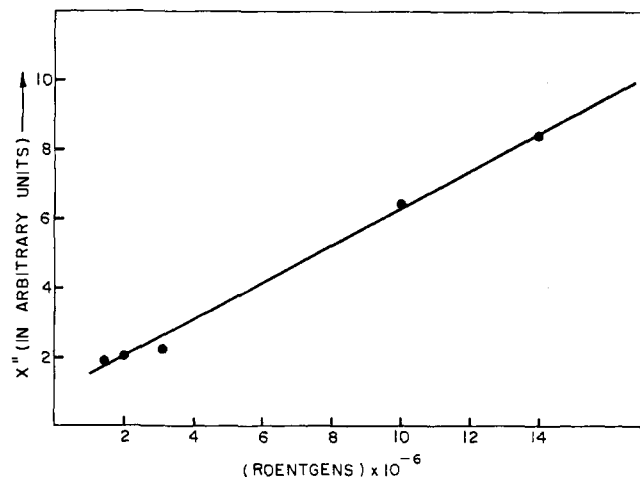


Fig. 2.—The increase of integrated spin susceptibility with dosage of γ -irradiation of NaY zeolite.

lites was found after irradiation of the diamagnetic activated samples. The width of this line measured between the points of maximum slope is about 38.4 gauss and has a g -value of 2.0200 ± 0.0002 . The e.s.r. absorption of this paramagnetic center is shown in Fig. 1A. After irradiation, the samples, particularly NaY, have an intense pink color.

The variation of the spin susceptibility (X) with dose rate of γ -irradiation is shown in Fig. 2. The number of paramagnetic centers increases with increasing dose rate. It appears that even at maximum irradiation ($\sim 1.4 \times 10^7$ roentgens), there is no indication that saturation of the crystal with γ -rays takes place. We shall refer to this resonance line (in the discussion to follow) as due to the X_1 center.

The shift of the spectroscopic splitting factor from the free spin value can be considered as an indication of

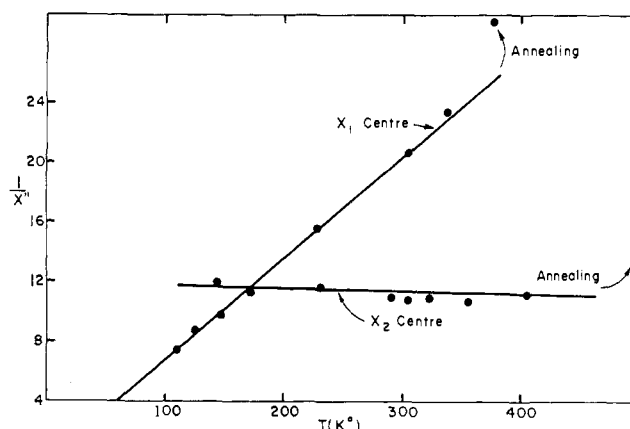


Fig. 3.—The reciprocal of integrated spin susceptibility for the two types of resonances of the X_1 and X_2 centers is plotted as function of absolute temperature.

the magnitude of the spin-orbit coupling of the unpaired electron. The shift, $\Delta g = g - 2.00229$, is negative for an unpaired electron and positive for a hole. The shift observed in the X_1 center is $\Delta g = 0.0177$ which is rather large and quite different from the free spin value. This indicates that the paramagnetic center responsible for the X_1 absorption line is a hole and not an electron. The absence of hyperfine structure in this line suggests that the hole is located far apart from the aluminum atom (Al^{27} , $I = 5/2$) and the Na ions (Na^{23} , $I = 3/2$). Otherwise, even through weak interaction of the hole with either of these magnetic nuclei, it should give some hyperfine structure. Further, the fact that the susceptibility increases with increasing γ -ray dosage indicates that there is not a limited number (at least for the maximum dosage used here) of sites which, through interaction with γ -rays, can become paramagnetic centers.

One could expect a saturation effect if the X_1 center was due to some kind of ionized impurity or lattice defect which traps electrons or holes. It appears then, that γ -irradiation produces paramagnetic defects in the aluminosilicate framework of the crystals. Before we discuss the nature of this center, some other observations have to be considered: First, the e.s.r. absorption of the X_1 center is very sensitive to O_2 . It was found that the line broadens with exposure to O_2 gas and this broadening is a function of the pressure of the O_2 gas in contact with that of the sample at room temperature. Near 500 mm. pressure the line was so broadened that it could not be detected. However, by pumping out this oxygen, the e.s.r. signal returns to its original intensity. The pink color also disappeared with absorption of O_2 . The amount of absorption of O_2 on these crystals at room temperature is very small and this is the reason why high pressure of O_2 is required before the e.s.r. line is completely eliminated.

However, the disappearance of the pink color with O_2 absorption does not effect the e.s.r. absorption line. For example, only a few mm. of O_2 pressure in the vacuum system is sufficient to bleach the sample. Nevertheless, this sample still exhibits an e.s.r. line which is only slightly broadened. The pink color also can be eliminated by adsorption of N_2 . Pumping out the N_2 , as in the case of O_2 , does not restore the color. On the other hand, nitrogen adsorption does not effect the e.s.r. line.

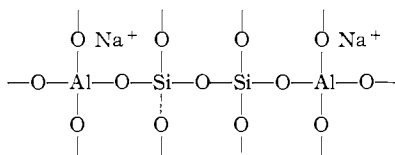
Second, the variation of spin susceptibility with temperature for this type of center, where the reciprocal of the spin susceptibility is plotted as a function of absolute temperature, is shown in Fig. 3. Below $350^\circ K$. the susceptibility changes reversibly with temperature

according to the Curie-Weiss law. The absence of a Weiss constant indicates that the centers do not interact and exist in a rather homogeneous dispersion in the lattice of the porous crystals.

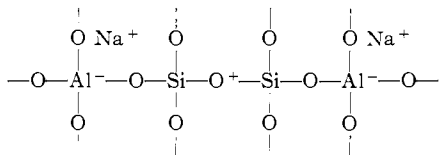
Above 350°K. the intensity of the e.s.r. decreases irreversibly, and near 450–500°K. the resonance line is eliminated completely. The effect of heating on the pink coloration of the samples is analogous to the effect of O₂ or N₂, discussed above. Namely, it requires heating for a short period of time at temperatures as low as 50° in order to decolorize the sample. Again, at this temperature, no observable changes take place in the e.s.r. absorption.

It is reasonable to assume that the pink color produced by the γ -irradiation of the crystals is not associated with the paramagnetic centers observed.

After having considered all these effects associated with the color and e.s.r. absorption, the following mechanisms are postulated for the pink color and for the e.s.r. signal. A segment of the aluminosilicate lattice can be represented by the simplified planar representation



In the NaY zeolite the ratio of SiO₂/AlO₂ is about 2.5 and one expects that on the average two consecutive (AlO_{4/2})⁻ units would be separated by two (SiO_{4/2}). The drastic degassing process used for the samples certainly eliminates all the water in the crystals so that the Na⁺ ions associated with the (AlO_{4/2})⁻ tetrahedra will produce rather high electrostatic fields in their vicinity. The magnitude of this type of field is reduced appreciably when the crystals contain absorbed water which, primarily through dipole-ion interaction, screens the charge on the Na⁺ ions. On considering the electrostatic field and field gradient in the (SiO_{4/2}) unit located next to the (AlO_{4/2})⁻ Na⁺, it appears unlikely that the γ -irradiation could create a stable electron hole around the (AlO_{4/2})⁻Na⁺ tetrahedron. Simple electrostatic considerations indicate that the presence of Na ions will hinder the stabilization of an electron hole in an adjacent (SiO_{4/2}) unit. It appears that a suitable site for the creation of an electron hole by γ -irradiation would be the region between the two adjacent (SiO_{4/2}) tetrahedra. This simplified picture indicates the hole



to be located between O¹⁶ and Si²⁴ atoms, neither of which have any nuclear magnetic moment.

We were not able to detect the free electron which is produced by the ionization of the oxygen atom. This was also the case for charge transfer complexes such as triphenylamine and iodine⁶ or, as will be discussed in a later paper⁷ for charge-transfer processes on the surface of zeolites. One of the reasons why this electron is undetectable by e.s.r. may be due to the fact that it becomes delocalized from the oxygen atom and migrates on the aluminosilicate lattice. In addition, the short relaxation times or local variations in the surrounding crystal field may so broaden the e.s.r. absorption line that it is not detected.

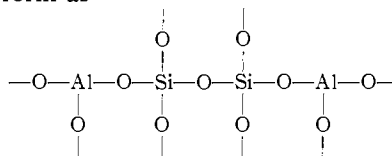
(6) D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 2557 (1963).

(7) D. N. Stamires and J. Turkevich, *ibid.*, in press.

The fact that a considerable low thermal energy is required to anneal the defect, and that (as will be shown later) this electron can be detected if trapped in a vacancy (after the lattice is modified) indicates that it is located in the lattice, even if not detectable there.

The pink color observed in the samples is probably associated with this electron. One possibility is that it might migrate to different locations in the polycrystalline sample where structural defects exist and, through interaction with such sites, give rise to this color. Another possibility is that these electrons located in the crystal cavities behave similarly to those found in ammonia solutions of sodium metal.⁸ In ammonia solutions of Na the volume increase has been associated with the electrons removed from the Na metal. The volume of the sphere enclosing the electron has been considered to be of the order of 100–150 Å.³ The volume of the cavities in the zeolite crystals are of the same order and the trapping of electrons in these spherical boxes is conceivable. The oxygen atoms which cover the interior surface of each cavity in the aluminosilicate network will have a strong polarization effect on the electrons trapped in them, and this effect of course, will modify the position of energy levels of the electrons located in the cavities. It is plausible that transition among these levels gives rise to the pink color observed. One could assume that the effects of the various gases, vapors, and temperatures on the pink color are due to the quenching of the small population of such electrons in an excited electronic state or their localization on an adsorbed gas molecule.

B. E.s.r. Absorption in Decationized NH₄X and NH₄Y Zeolites.—When the NH₄Y zeolite is heated under vacuum near 500°, the NH₄⁺ ions are decomposed to give NH₃ and H⁺ which in turn are eliminated in the form of water after one oxygen atom is abstracted for every two H⁺. This process, which is discussed in detail elsewhere,⁸ transforms the four-coordinated aluminum to the three-coordinated state. The lattice of the crystals after decationization can be represented in a simplified form as



The e.s.r. absorption of a 90% exchange NH₄Y sample after decationization is shown in Fig. 1B. We shall refer to this e.s.r. absorption as due to the X₂ center. The *g*-factor is 2.001 which gives Δg from the free electron a value of -0.001. It is of interest to note that a similar shift has been observed in ammonia solutions of Na metal.⁶

In the hyperfine structure observed, six lines can be distinguished which are assumed to be due to the interaction of a trapped electron with the nuclear moment of the Al²⁷ (*I* = 5/2). The anisotropy in the hyperfine structure is attributed to the fact that we are using polycrystalline samples which tend to obscure well defined anisotropies in the *g* or in the hyperfine interaction tensors which are easily resolved when single crystals are used. However, the *A* near the center of the hyperfine structure is about 5 gauss (4.7 × 10⁻⁴ cm.⁻¹). It is of interest to note that some similar hyperfine splittings have been observed¹ in the X-irradiated Al containing quartz crystals. The small hyperfine structure was resolved only at 20°K. and the spectrum was fitted to the spin Hamiltonian

$$\mathcal{H} = HgS + A_x S_x I_x + A_y S_y I_y + p[I_z^2 - \frac{1}{3}I(I + 1)] - \gamma\beta\mu HI$$

(8) T. Kaplan and C. Kittel, *J. Chem. Phys.*, **21**, 1429 (1953).

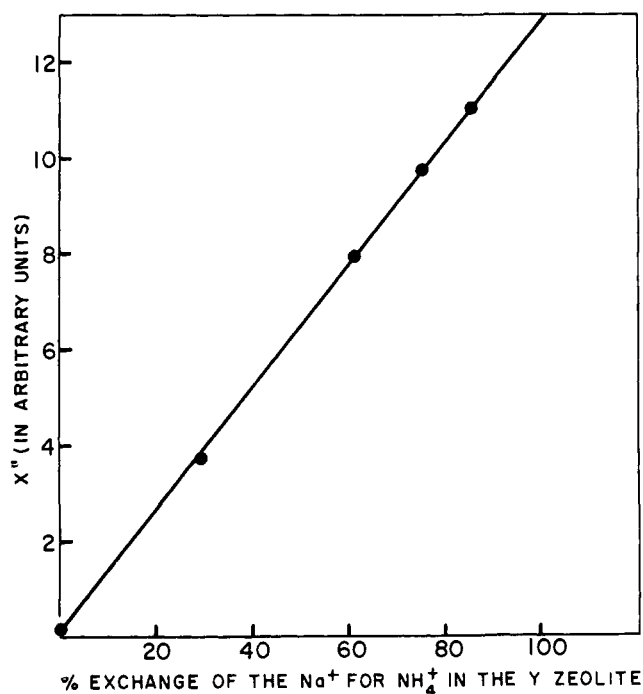


Fig. 4.—The variation of the integrated spin susceptibility with % decationization of the Y zeolite.

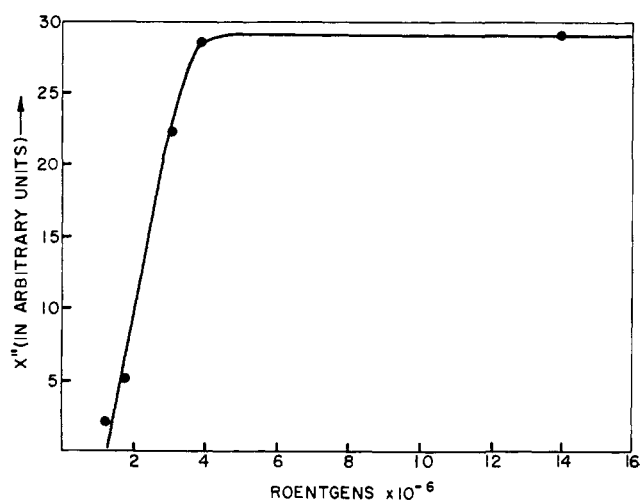


Fig. 5.—The increase of integrated spin susceptibility with dosage of γ -irradiation of decationized Y zeolite.

where the g -tensor has principal values of $g_{\parallel} = 2.06 \pm 0.005$ and $g_{\perp} = 2.00 \pm 0.005$. The hyperfine structure constants are $A_z = 4.8 \times 10^{-4} \text{ cm.}^{-1}$, $A_x = A_y = 5.6 \times 10^{-4} \text{ cm.}^{-1}$, and the quadruple interaction constant $P = 4 \times 10^{-5} \text{ cm.}^{-1}$. The principal axes of the hyperfine structure (XYZ) are not the same as the axes of the g -tensor. This produces six electronic absorption lines, each with six hyperfine structure components.

The spectrum of the irradiated decationized zeolite showed no such anisotropy of the g -tensor in the temperature range studied (300–77°K.). The A obtained for the irradiated zeolite, $4.7 \times 10^{-4} \text{ cm.}^{-1}$, is comparable to those found for the irradiated quartz. However, the e.s.r. absorption of the zeolite is quite different from that found in the quartz.

First, the hyperfine structure is observed at room temperature and cooling to 77°K. has no appreciable effect. On the other hand, the resonance in the irradiated quartz is observed only at 20°K. Second, hyperfine structure was observed in the zeolite only

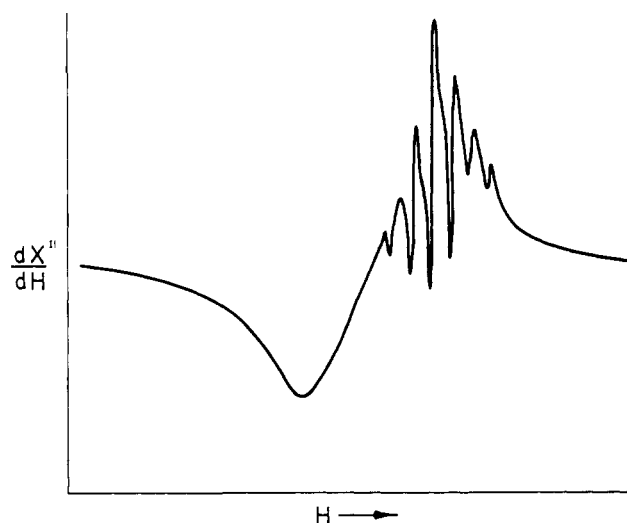


Fig. 6.—E.s.r. of X_1 and X_2 centers in a partially decationized zeolite.

when some of the cations were eliminated and the associated aluminum atoms were accordingly changed from the four- to three-coordinated state. In the case of quartz, hyperfine structure was explained as due to a hole associated with the Al atom in the four-coordinate state in the silicate lattice. However, there is no experimental evidence that the Al atoms are in a four-coordinate state in the quartz crystal. This is mainly due to the fact that the Al is present as small amounts of impurities which make it difficult to determine the amount of cations present, especially if protons are present. The intensity of the resonance absorption in the irradiated decationized zeolite increases with the increasing number of decationized sites in the crystal. This is shown in Fig. 4 where the integrated absorption intensity is plotted as a function of the numbers of Na⁺ exchanged for NH₄⁺ before heating the samples. The linear variation indicates that the number of trapped electrons follows the increase of the number of three-coordinated alumina. However, a comparison of the number of spins with the number of three-coordinated alumina is not possible at the present time, since the samples were irradiated at room temperature and a time decrease in the signal intensity was observed (the maximum susceptibility in Fig. 4 corresponds to about 2×10^{17} spins/g.). The variation of spin susceptibility with dosage of γ -irradiation is shown in Fig. 5. Above 4×10^6 roentgens the susceptibility becomes independent of the amount of irradiation. This is typical behavior for cases where the irradiation ionizes existing defects in the solid. This effect is quite different from that observed in the case of the X_1 center.

For resonance associated with the X_2 center no variation of the absorption intensity with temperature changes was found in the region between 400–150°K. as shown in Fig. 3.

However, above 200° the intensity irreversibly decreases slowly up to 500° where the annealing is completed. The structure at the lower temperature becomes increasingly anisotropic and this makes it rather difficult to detect small changes in the intensity. Nevertheless, it is obvious that the behavior of the X_2 is quite different from that of the X_1 center. Certainly, if this temperature-independent behavior of the X_2 center is true, it is not easily understood. One could expect the susceptibility to be independent of temperature if the trapped electrons were located in a conduction band in the crystal lattice. However, this is difficult to

imagine when there is hyperfine structure in the e.s.r. absorption of these electrons.

C. E.s.r. Absorption in the Y Zeolite Containing Both $\text{Na}(\text{AlO}_{4/2})$ and $(\text{AlO}_{3/2})$ Units.—So far we have considered the two extreme cases observed in the e.s.r. of irradiated NaY zeolite and decationized Y zeolite. As was mentioned previously, the NaY zeolite gave a single ($g = 2.002$) absorption line, whereas the ($\sim 90\%$ decationized) exhibited hyperfine structure (center at $g = 2.0017$). In addition to these two extreme cases there is another intermediate case where, by having a sufficient number of $(\text{AlO}_{3/2})$ together with the Na^+ $(\text{AlO}_{4/2})^-$ sites, both signals (due to X_1 and X_2 centers) can be observed simultaneously. This is illustrated in Fig. 6 for a sample containing 35 $(\text{AlO}_{3/2})$ and 21 Na^+ $(\text{AlO}_{4/2})^-$ units per unit cell of the crystal. The intensity of the line with the hyperfine structure, as was mentioned above, increases with increasing degree of decationization.

It appears then, that the three-coordinated aluminum in the crystal lattice acts as an electron sink where the electrons are trapped.

The X_1 center in the NaY zeolite was assumed to be a hole associated with the $(\text{SiO}_{4/2})$. The electrons produced by the ionization of the oxygen atoms in order to produce these holes cannot be observed by e.s.r. and this may be due to the delocalization and mobility of these electrons located in the crystal cavities. However, the localization of those electrons by trapping them in $(\text{AlO}_{3/2})$ sites make it possible to observe an e.s.r. absorption.

It is quite interesting to point out here that the intensity of the pink color varies also with the degree of decationization. For example, an irradiated 100% NaY is deeply colored pink; the intensity of coloration decreases as decationization increases. The 90% decationized sample is completely colorless. This effect of removing the color by trapping can be compared with the parallel quenching effect of absorbed O_2 . It appears that the trapping of the electrons decreases the population in the excited energy levels of these electrons in the crystal cavities.

The above-postulated model for the X_1 and X_2 centers explains the following observations: First, the annealing temperature of the X_2 center is much higher than for the X_1 . One would expect that the energy of the electron located in the zeolite cavity would be much less than when trapped in the $(\text{AlO}_{3/2})$ unit. Second, absorbed oxygen broadens the e.s.r. line of the X_1 center, but it does not affect that of the X_2 center. This is due to the easy approach of the O_2 molecules to the holes located on the oxygen atoms of the lattice which are easily accessible to the entering gaseous molecules. However, the trapped electrons located near the Al atoms in the $(\text{AlO}_{3/2})$ units are much less easily reached by the absorbed O_2 molecules. It is known that oxygen cannot reach the smaller cavities in the synthetic zeolites.

D. The Electron-Accepting Properties of the Three-Coordinated Unit in the Decationized Y Zeolite.—It has been found previously that decationized Y zeolite absorbs molecules with electron-donating properties and in this absorption process an electron is transferred from the absorbed molecules to the zeolite lattice (e.g., triphenylamine $(\text{C}_6\text{H}_5)_3\text{N}$ absorbed from *n*-heptane solution) or the zeolite transfers an electron to the ac-

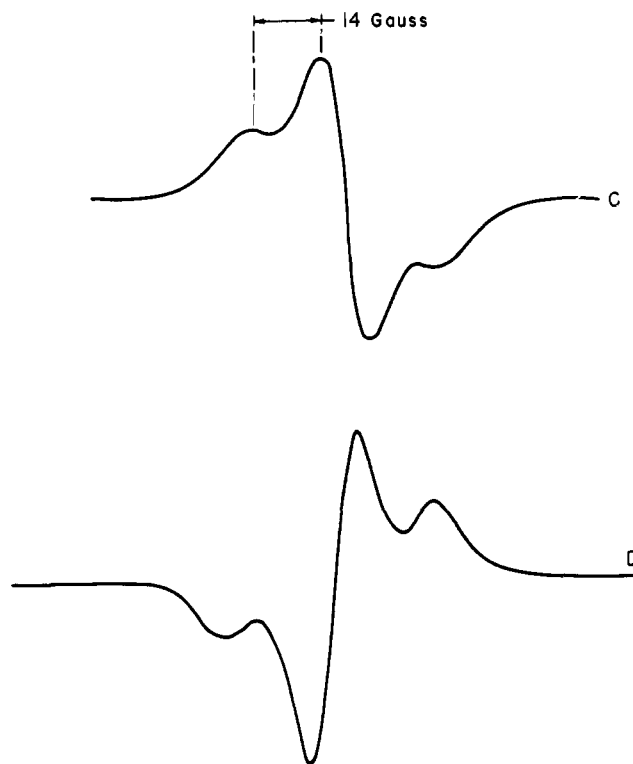


Fig. 7.—E.s.r. of $[(\text{C}_6\text{H}_5)_3\text{N}^+]$ cation radical formed on decationized zeolite at room temperature (C). The spectrum of $(\text{C}_6\text{H}_5)_3\text{N}$ and I_2 charge-transfer complex is shown in D.

ceptor unit $(\text{AlO}_{3/2})$ and the complex $[(\text{C}_6\text{H}_5)_3\text{N}^+][\text{AlO}_{3/2}]^-$ is formed. The three peaks found are due to the interaction of the unpaired electron with the nucleus of the N^{14} atom. The electron-donating properties of the $(\text{C}_6\text{H}_5)_3\text{N}$ were demonstrated previously,⁷ as for example with I_2 , forming the complex $[(\text{C}_6\text{H}_5)_3\text{N}^+][\text{I}_2]^-$.

The $(\text{AlO}_{3/2})$ acceptor in the lattice takes up electrons from donor molecules or traps electrons from the ionizing effects of the γ -irradiation discussed above. This is indicated by the fact that the γ -irradiated decationized zeolite which shows a strong resonance with the six-line hyperfine structure, when contacted by $(\text{C}_6\text{H}_5)_3\text{N}$ in solution, does not accept any electrons from the $(\text{C}_6\text{H}_5)_3\text{N}$. It appears that the sites at which the electrons are transferred from $(\text{C}_6\text{H}_5)_3\text{N}$ are already occupied by trapped electrons produced by γ -irradiation. Hence the e.s.r. and the color of the γ -irradiated decationized zeolite are not affected by contact with a *n*-heptane solution of triphenylamine.

However, if the six-line resonance is annealed and the e.s.r. completely eliminated, the triphenylamine absorption results in electron transfer and the e.s.r. absorption. It appears that the $(\text{AlO}_{3/2})$ site in the crystal framework will trap electrons either from donor molecules or from ionizing irradiation.

Acknowledgment.—We wish to acknowledge the financial support of the United States Atomic Energy Commission, the radiation facilities of the RCA Laboratories at the Industrial Reactor Laboratories at Plainsboro, N. J., and the technical assistance of George Kemmerer.