

Paramagnetic Nitrogen Oxides in Irradiated Potassium Halides*

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In x-ray irradiated single crystals of KCl, KBr, and KI doped in the melt with nitrate or nitrite, six triplets and one singlet are observed in electron paramagnetic resonance between -190°C and room temperature. The trapping mechanism producing the centers is indicated by the behavior of the electron paramagnetic resonance signal during optical or thermal release of free electrons (from F centers) or holes (from Cl_2^-), and the chemical nature of the centers by selective doping methods. In all three salts these tests have identified NO interstitials (anisotropic up to room temperature, almost axial symmetry, principal paramagnetic axes in $[100]$, $[011]$, and $[0\bar{1}1]$ directions); NO in positive-ion va-

cancies (isotropic); and NO_3^{--} in negative-ion vacancies (anisotropic below -145°C , axial symmetry, axis in $[111]$ direction). In KCl and KBr, NO_2^{--} in negative-ion vacancies (anisotropic, axial symmetry, axis in $[110]$ direction, visible below -125°C), and oxygen molecules (anisotropic, almost axial symmetry, axes in $[100]$, $[011]$, $[0\bar{1}1]$ directions, visible below -100°C) have been identified. Information regarding the bonding in the molecules has been obtained. Two isotropic triplets are not identified. The relative concentrations are different in the various host crystals, and the linewidth increases according to the halogen nuclear moment.

I. INTRODUCTION

THE addition of a small concentration of nitrate or nitrite to the melt of alkali halides modifies the optical absorption, with indication that the foreign ions are substituted into regular lattice sites as impurities. Early experiments by Maslakowicz¹ showed that a chemical dissociation of the impurities takes place in the melt and that an equilibrium between NO_2^- and NO_3^- results, which is determined by the melting point of the host crystal. In irradiated doped crystals, Hutchinson and Pringsheim² discovered absorption bands in the visible and ultraviolet spectrum connected with the presence of NO_2^- , but their results could not be interpreted with certainty.

The purpose of this work was to obtain by the method of electron paramagnetic resonance (EPR) more detailed information on the included impurities in KBr and KI and the effect of x or gamma rays. Although preliminary investigations indicated the presence of two paramagnetic centers only, further experiments were complicated by the detection of seven different centers, many of them being anisotropic and occurring together. After a description of the experimental procedures, the results and their interpretation are given for the centers in KCl and compared with those of KBr and KI.

II. EXPERIMENTAL

The crystals used in the experiments were single crystals either purchased from the Harshaw Chemical Company or grown in this laboratory from Reagent grade potassium halides. Certain crystals were doped in the melt by adding 0.01 to 1 weight percent NaNO_3 or KNO_2 to the pure powder, and then the single crystals were produced in quartz or Pt crucibles by either the Kyropoulos or the Bridgman method. Other samples

cleaved from large single crystals of pure KCl were sealed in a quartz tube which had been evacuated and filled with $\frac{2}{3}$ atm distilled NO_2 . The tube was heated to 700°C for periods ranging from 1 to 20 days. Because of the high temperature, the nitrogen dioxide was almost completely decomposed into nitric oxide and oxygen, so that a surface layer of $\frac{1}{2}$ mm thickness or more was doped with NO and O_2 . An attempt was made to have only NO by filling the tube (after evacuation) with this gas which had been purified once through vacuum distillation. However, the NO must react at high temperature, because the characteristic brown color of NO_2 appears when the tube is cooled down to room temperature. To eliminate a high steady-state concentration of NO_2 , the crystals were heated in an open tube where NO was flowing slowly, removing the reaction products.

To eliminate the effects of anisotropic centers, certain crystals were ground with an agate mortar in a dehumidified glove box, and then compressed in a steel mold with an hydraulic press (20 tons) to give a transparent, polycrystalline pellet of 6-mm diameter and 1-mm thickness. These pellets, as well as the single crystals, were examined with a Perkin-Elmer infrared spectrograph to check the relative amount of NO_2^- and NO_3^- included in the lattice, each one of these ions giving a sharp characteristic absorption peak at $7.85\ \mu$ and $7.22\ \mu$, respectively.¹ For short times, ranging from 15 sec to 30 min, the samples were irradiated with x rays from a Machlett x-ray tube (50 kv, 50 ma tungsten target) at a distance of 1 in. from the tube window, or for longer times with a Co^{60} source of 4 kC.

The resonance measurements were performed with a Varian EPR spectrometer model V4500, with 100 kc/sec field modulation, and a 6-in. electromagnet V-4007-1. Through the use of a variable temperature device V-4547 (gas cryostat) and a Dewar vessel, measurements were made from liquid nitrogen up to room temperature. A copper-constantan thermocouple, placed below the sample in the cold gas stream, measured the temperature which was stabilized manually within 5°C . The microwave frequency was measured with a Hewlett

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¹ I. Maslakowicz, *Z. Physik* **51**, 696 (1928).

² E. Hutchinson and P. Pringsheim, *J. Chem. Phys.* **23**, 1113 (1955).

TABLE I. Paramagnetic centers in KCl. $A/g_e\beta_e$, $B/g_e\beta_e$, $C/g_e\beta_e$, and W (width at half height of the absorption line) in gauss; the brackets indicate the crystallographic orientation of the principal tensor axes.

No.	Center	$T(^{\circ}\text{C})$	g_z	g_x	g_y	$A/g_e\beta_e$	$B/g_e\beta_e$	$C/g_e\beta_e$	W
1	NO int.	-15 -50	2.0038 ± 0.0002 [100]	2.0070 ± 0.0004 [011]	2.0099 ± 0.0002 [011]	32.5 ± 0.2 [100]	4.9 ± 0.3 [011]	4.9 ± 0.3 [011]	1.0 ± 0.1
2	NO+[+]	0		2.0069 ± 0.0002			14.2 ± 0.2		2.8 ± 0.2
3	NO ₃ ²⁻ +[-]	-190 0	2.0020 ± 0.003 [111]	2.0068 ± 0.0002 2.0052 ± 0.0002		61.5 ± 0.5 [111]	30.5 ± 0.2 40.2 ± 0.2		12.0 ± 0.5 5.2 ± 0.4
4	NO ₂ ²⁻ +[-]	-190	2.0014 ± 0.0002 [110]	2.0003 ± 0.0003		43.2 ± 0.5 [110]	62.5 ± 0.5		2.4 ± 0.2
5	O ₂ ⁺ + [+]	-190	2.0422 ± 0.0002 [100]	2.0029 ± 0.0002 [011]	2.0099 ± 0.0002 [011]	0	0	0	1.75 ± 0.15

Packard Cavity Wavemeter (X532B). A Micro-Now microwave frequency calibrator (type 101, accuracy 1 in 10^5) was connected to the bridge through a unidirectional coupler and gave a reference signal consisting essentially of the harmonics of 450 Mc/sec, with smaller intensity in those of 150, 50, 25, and 5 Mc/sec; the spectrometer detecting unit indicated when the klystron frequency (changed slowly by varying the reflector voltage) was 100 kc/sec off one of the harmonics generated by the calibrator, practically every 5 Mc/sec, and permitted calibration of the wavemeter, with an absolute accuracy of 0.5 Mc/sec. The magnetic field was measured with a Harvey-Wells NMR gaussmeter G 501; in comparing its 15 Mc/sec marker with the 15-Mc/sec harmonics of the microwave calibrator, an accuracy of 0.15 gauss could be obtained. The lowest error for g factors is thus ± 0.0002 , for a narrow well-revolved line.

III. RESULTS AND DISCUSSION

No resonance has ever been found in crystals before irradiation, indicating the inclusion of the nitrogen compounds in the form of diamagnetic species (or of paramagnetic species with very short relaxation times). The concentration of the observed centers ranged from 10^{15} to 10^{18} cm⁻³, and the paramagnetic properties are summarized in Table I for KCl. With the exception of the last one, which is a singlet, all are triplets and involve a nitrogen nucleus; this has been checked by substituting N^{15} ($I=\frac{1}{2}$) for N^{14} ($I=1$), the triplets reducing then to doublets and the ratios of the splittings agreeing exactly with the values of the nuclear moments. The line shape is (with exception of center 3) nearly Gaussian and the width at half height of the absorption line is given in the last column.

As no quadrupole effects have been observed, the Hamiltonian describing the centers has the conventional form:

$$-\mathcal{H} = \beta_e(g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) + AS_z I_z + BS_x I_x + CS_y I_y. \quad (1)$$

The g and hfs tensors were observed to have the same principal axes; g_z and A refer to the rotation axis, if present, or to the axis with larger hfs or g . The squares of the g factor and of the hfs are always linear functions of $\cos^2\theta$, where θ is the angle between the magnetic field and the axis of symmetry. Thus, according to Zeldes *et al.*,³ the splitting in the case of a rotation symmetry for the electronic distribution can be interpreted for sp orbitals as

$$A = g_e \beta_e g_N \beta_N [(8\pi/3)|\psi(0)|^2 + \langle(3\mu^2-1)/r^3\rangle], \quad (2)$$

$$B = g_e \beta_e g_N \beta_N [(8\pi/3)|\psi(0)|^2 - \frac{1}{2}\langle(3\mu^2-1)/r^3\rangle]. \quad (3)$$

where g_N , β_N are the nuclear g factor and magneton, $|\psi(0)|^2$ the electron density at the nucleus, and μ the cosine of the angle between the electron radius vector r and the rotation axis z . As the signs of A and B are not known, one has the choice between two solutions for $|\psi(0)|^2$ and $\langle(3\mu-1)/r^3\rangle$, satisfying the condition that $|\psi(0)|^2 > 0$.⁴

$$|A| > |2B|:$$

$$\begin{aligned} \frac{3}{2}\langle(3\mu^2-1)/r^3\rangle &= (|A| \pm |B|)/g_e \beta_e g_N \beta_N; \\ 8\pi|\psi(0)|^2 &= (|A| \pm 2|B|)/g_e \beta_e g_N \beta_N. \end{aligned} \quad (4)$$

$$|A| < |2B|:$$

$$\begin{aligned} \frac{3}{2}\langle(3\mu^2-1)/r^3\rangle &= (\pm|A| - |B|)/g_e \beta_e g_N \beta_N; \\ 8\pi|\psi(0)|^2 &= (\pm|A| + 2|B|)/g_e \beta_e g_N \beta_N. \end{aligned} \quad (5)$$

The uncertainty can be listed in all the cases shown later.

It is important to test if the centers are produced by electron or hole trapping, and there are two complementary methods. In the first one, the F centers of the regular lattice are bleached with 560-m μ light; the electrons are then released into the conduction band and trapped by the impurities. Such an impurity, which was diamagnetic, becomes then paramagnetic, and the

³ H. Zeldes, G. T. Trammell, R. Livingston, and R. W. Holmberg, J. Chem. Phys. **32**, 618 (1960).

⁴ In the case of exchange polarization with negative s contribution occurring with pure p orbitals, both Eqs. (4) and (5) have to be considered.

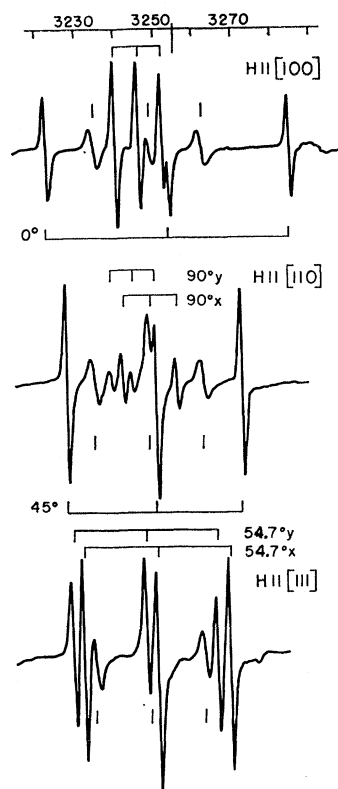


FIG. 1. EPR spectrum of NO in KCl, for different crystal orientations in the magnetic field. The three isotropic lines are produced by NO in positive ion vacancies; the brackets refer to the lines of NO interstitials with indication of the angle between the molecular axis and the field. (Upper scale in gauss; frequency: 9125 Mc/sec).

intensity of the corresponding EPR spectrum increases; if the impurity was already paramagnetic, the trapped electron pairs with the odd one, and the corresponding spectrum intensity decreases. In the second method, the crystal is irradiated and measured at a temperature lower than -80°C , to keep the holes trapped in Cl_2^- ions.⁵ Upon heating, the holes are liberated into the lattice, trapped by the impurities, and produce inverse effects. At low temperatures, the presence of an electron acceptor impurity in sufficient concentration inhibits almost completely the formation of F centers and thus the EPR spectrum consists of Cl_2^- ions and species resulting from the trapping of electrons.

A. NO in KCl

The first of the centers in Table I (Fig. 1) has already been described⁶; it is anisotropic and stable up to room temperature, where it decays irreversibly within half an hour. The g values are independent of the temperature, but the hfs parameters show a little variation; the slight deviation from rotation symmetry disappears below -150°C . At this point, one observes saturation broadening with the microwave power greater than 10 mw, and at -190°C , the high field line for $\theta=0$ broadens by about a factor of two.

This center is present in small amounts in crystals

doped from the melt, but its relative concentration is greatly enhanced in a pure crystal heated in NO_2 gas (i.e., a mixture of NO, NO_2 , and O_2) or in pure NO gas.

The second center is isotropic, the g value and the hfs showing no dependence of the temperature. The lines narrow from 2.8 to 1.8 gauss from 0° to -100°C and saturate progressively upon further cooling. The center disappears at room temperature within three hours. It is always present with the first one, the intensity ratio being constant in crystals heated in NO_2 or NO. Moreover, the g value of the isotropic one is equal to the space average value of the anisotropic one, and if we transform our results with Eq. (4) we obtain:

Center 1:

$$|\psi(0)|^2 = 0.84 \times 10^{24} \text{ cm}^{-3} \quad \langle 1/r^3 \rangle = 11.5 \times 10^{24} \text{ cm}^{-3} \quad (0.45) \quad (15.5)$$

Center 2:

$$|\psi(0)|^2 = 0.85 \times 10^{24} \text{ cm}^{-3} \quad \dots$$

The magnetic electron-nucleus coupling in the free NO molecule has been calculated from previous measurements by Dousmanis,⁷ yielding the values $|\psi(0)|^2 = 0.85 \times 10^{24} \text{ cm}^{-3}$ and $\langle r^3 \rangle = 14.9 \times 10^{24} \text{ cm}^{-3}$; using another model, Mizushima⁸ obtains $|\psi(0)|^2 = 1.02 \times 10^{24} \text{ cm}^{-3}$. If we drop the second solution for center 1, we get a good agreement between these results, and this suggests that both centers are due to NO in the same electron configuration but in different locations.

They are both produced by electron trapping; the EPR signal of the first one increases if the F centers formed in the regular lattice are bleached with green light at room temperature, this being accompanied by a very fast decoloring of the surface zone in which the NO has diffused. The signal intensity of the second center increases also upon F bleach and decreases upon thermal decomposition of the Cl_2^- in a crystal irradiated at low temperature.

In a simple interpretation agreeing with the experimental facts, the NO molecules are included in the lattice in the form of nitrosyl chloride in a vacancy pair ($\text{NOCl} [+][-]$), or in a negative-ion vacancy ($\text{NOCl} [-]$). During irradiation, $\text{NOCl} [+][-]$ traps an electron to become a regular Cl^- plus a neutral NO molecule in the positive-ion vacancy; the internuclear distance N—O is 1.14 Å, and the diameter of the vacancy is 2.66 Å. Its small dipole moment (0.15 debye⁹) does not prevent the NO from rotating despite the crystalline field, but not completely freely; the orbital moment is quenched; and only the s component of the odd electron wave function is revealed by the hfs. Having trapped an electron, $\text{NOCl} [-]$ becomes a NOCl^- which dissociates, the chlorine ion going in the negative-ion vacancy, and the NO molecule remaining

⁵ T. G. Castner, W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957); P. Yuster, C. Delbecq, Phys. Rev. **111**, 1235 (1958).

⁶ C. Jaccard, Bull. Am. Phys. Soc. **5**, 418 (1960).

⁷ G. C. Dousmanis, Phys. Rev. **97**, 967 (1955).

⁸ M. Mizushima, Phys. Rev. **105**, 1262 (1957).

⁹ C. A. Burrus and J. D. Graybeal, Phys. Rev. **109**, 1553 (1958).

as an interstitial. There is enough room if the NO is in the $[100]$ direction; the distance N—Cl or O—Cl is 2.44 Å, which leaves a free radius of 0.64 Å around the N or O nuclei. However, the molecule has no room to rotate and it is locked in its $[100]$ orientation.

In optical experiments, the bleaching of the F centers increases the number of the anisotropic species by a factor of 5 or more, but the isotropic one at most by a factor of 1.5; this greater electron affinity of the interstitial NO can be explained by the fact that the system (NOCl plus negative-ion vacancy) is positively charged with respect to the regular lattice, whereas the system (NOCl plus vacancy pair) is not.

In the free NO molecule, the odd electron is essentially in a $p\pi$ antibonding state.^{7,8} For the interstitial molecule, the proximity of the Cl^- ions would repel the $p\pi$ wave functions, and the g factor would be much more influenced by the crystalline field; thus, the odd electron is likely to be in a $p\sigma$ state, leaving, as observed, the g_z almost equal to the free electron value, and the g_x and g_y slightly larger, as is the case for the (halogen)₂⁻ molecule ion also in a $p\sigma$ state. The fact that the g factor and the hfs of the NO in the positive-ion vacancies equal the space averages of those of the interstitial NO suggests that both NO molecules have the same electronic configuration. That the freely rotating NO appears to be in a $p\sigma$ state rather than in the $p\pi$ state of the free molecule is surprising.

B. NO_3^{--} in KCl

The two systems of the third center of Table I (Fig. 2) are connected: When the temperature decreases, the isotropic system disappears at -140°C and the anisotropic one appears below -145°C ; moreover, during bleaching and heating experiments performed on the same crystal, the intensity ratio is always the same. An examination of the g values reveals that the isotropic g is equal to the space average of the anisotropic one. This suggests that both systems belong to the same center, which is oriented below -145°C but rotates above this temperature.

The isotropic system saturates at low temperature for microwave power greater than 10 mw, the linewidth increasing 1 gauss from room temperature to -100°C , but the anisotropic one does not vary appreciably with the temperature; its absorption lines are neither Gaussian nor Lorentzian, but with a broad top, concealing certainly an unresolved structure.

The center is present in all the samples, but with a relatively lower intensity in single crystals heated in NO gas. In KCl pellets containing only KNO_3 , pressed and heated up to 200°C to increase the diffusion, only a sharp NO_3^- line is observed in the infrared spectrum, indicating a predominant amount of nitrate ions included in the lattice, while the EPR shows only the isotropic spectrum characteristic of this center. Thus, the center is likely to be a neutral or doubly charged

nitrate ion (NO_3 , NO_3^{--} , or NO_3^{++}). The following observation leads to the assumption that the center is produced by electron trapping: In irradiated KCl (NO_3^-) powder, the formation of Cl_2^- is not at all inhibited at low temperature, and if the holes are released by heating, the EPR signal intensity of the center decreases by a factor of two or three.¹⁰

A plausible model consists of a NO_3^{--} in a negative-ion vacancy, trapping an electron during irradiation, to give a NO_3^{--} . Each oxygen, (with a net negative charge) is bound with a single $p\sigma$ bond to the nitrogen (with a net positive charge); the odd electron is in a three-electron $p\pi$ bond resonating between the three oxygens and the nitrogen, with the lobes of the p functions parallel to the molecular axis. If the NO_3^{--} were planar, then no s - p hybridization could occur for an odd electron in a π state (because of reflection symmetry, $p\pi$ being odd and s even). Therefore, the isotropic hfs could only occur by exchange polarization; in that case, it would be small and negative, in contradiction to the experimental results. We conclude that the NO_3^{--} is not planar. Experimentally, the rotation axis of the g and hfs tensors is in the $[111]$ direction; this indicates that the p functions point also in this direction. In the (111) plane (Fig. 3),

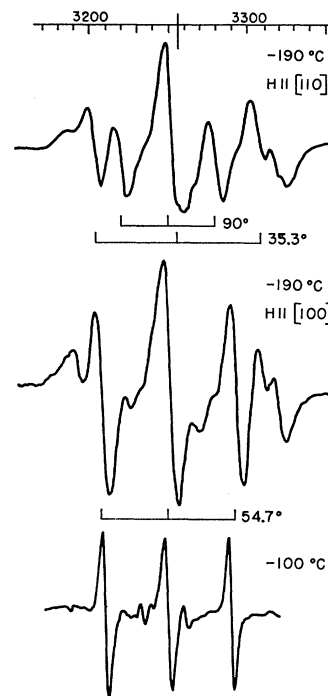


FIG. 2. EPR spectrum of NO_3^{--} in KCl, for two crystal orientations in the magnetic field at -190°C , and for -100°C , with indications of the angle between the molecular axis and the field. (Upper scale in gauss; frequency: 9125 Mc/sec.)

¹⁰ This supports the hypothesis that the center is not produced by nitrate radiolysis: If it were NO_2 [J. Cunningham, J. McMillan, and B. Smaller (to be published)] it would become NO_2^+ upon hole trapping; this could obviously occur only if located in a positive-ion vacancy; then (without introducing a much more complicated mechanism with vacancy pair and/or place change) the primitive NO_3^- should also be in a positive-ion vacancy, which is quite improbable. Moreover, the center would also occur in NO_2^- -doped pellets, which is not the case.

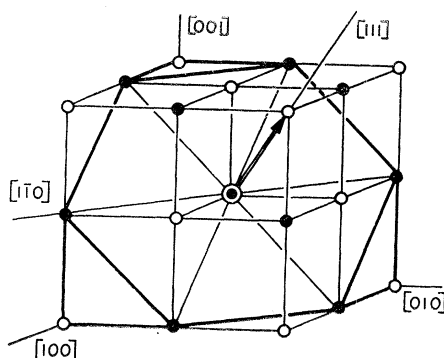


FIG. 3. Environment of the NO_3^{--} ion in the (111) plane (white circles: cations; black circles: anions).

the NO_3^{--} is surrounded hexagonally by 6 chlorine ions, 4.45 Å distant, and trigonally by two sets of three potassium ions, one on each side of the plane at a distance of 3.14 Å. These neighboring ions are certainly responsible for the odd line shape, resulting from many unresolved hyperfine lines.

A transformation of the experimental parameters with Eq. (4) yields

$$|\psi(0)|^2 = 2.44 \times 10^{24} \text{ cm}^{-3}, \quad (0.01)$$

$$\langle (3\mu^2 - 1)/r^3 \rangle = 10.3 \times 10^{24} \text{ cm}^{-3}, \quad (30.6)$$

and $|\psi(0)|^2 = 2.41 \times 10^{24} \text{ cm}^{-3}$ for the isotropic center, so that the second solution can be disregarded; the odd electron has thus a relatively large amount of s character, about three times as much as in NO.

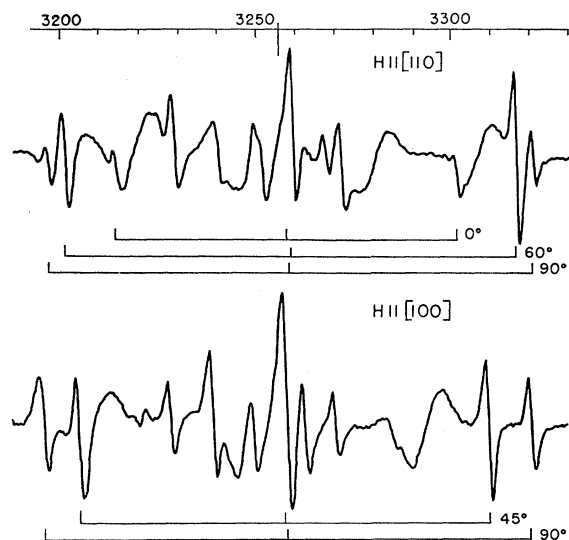


FIG. 4. EPR spectrum of NO_2^{--} in KCl, for two crystal orientations in the magnetic field. The position of the lines is indicated by the brackets, with the angle between the molecular axis and the field. The lines in the middle part of the spectrum belong to other centers described in this paper. (Upper scale in gauss; frequency: 9125 Mc/sec.)

At temperatures higher than -140°C the center changes its orientation swiftly enough to smear out the dipolar interaction and reveals only the isotropic part of the tensors, as the vacancy radius is 1.8 Å and the N—O distance only about 1.2 Å; below -145°C , this movement is greatly reduced, but it is possible that the rotation around the molecular axis persists down to low temperatures.

C. NO_2^{--} in KCl

Center 4 (Fig. 4) is formed only in crystals doped in the melt and apparently in powders ground with KNO_2 and heated up to 400°C , revealing in the infrared the presence of NO_2^{--} ions only. Thus, it is likely to be related to the nitrogen dioxide.

The EPR spectrum is visible only below -125°C , and disappears in a reversible way if the temperature is raised less than 100°C above this point. No isotropic component has been found at higher temperature, in contrast to the NO_3^{--} . As the EPR signal increases if free electrons are released in the crystal, it seems probable that center 4 consists of a NO_2^- in a negative-ion vacancy, trapping during irradiation an electron to

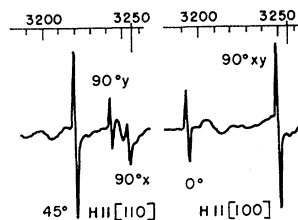


FIG. 5. EPR spectrum of oxygen in KCl, with two crystal orientations in the magnetic field, and indications of the angle between the molecular axis and the field (scales in gauss; frequency: 9125 Mc/sec.)

become an NO_2^{--} ; NO_2 and NO_2^- are not linear; it is plausible that the addition of another electron increases the ONO angle but without producing a linear NO_2^{--} molecule ion. The odd electron is certainly in a p state in the nitrogen atom. If we assume that the molecule and, therefore, the p lobe are fixed in space, then $\langle (3\mu^2 - 1)/r^3 \rangle$ must be positive; but the calculation from the observed hfs then yields negative values for $|\psi(0)|^2$ which are much too large to account for an exchange polarization. On the other hand, one can obtain a solution of Eq. (5):

$$|\psi(0)|^2 = 3.34 \times 10^{24} \text{ cm}^{-3},$$

$$\langle (3\mu^2 - 1)/r^3 \rangle = -6.4 \times 10^{24} \text{ cm}^{-3},$$

with a reasonable positive value for $|\psi(0)|^2$; then the negative sign of $\langle (3\mu^2 - 1)/r^3 \rangle$ must be interpreted by a rotation of the molecule, with the axis perpendicular to the odd electron p lobe. Moreover, the s admixture implies that the odd electron is not in a $p\pi$ state (which has other reflection symmetry than s), but in a $p\sigma$ state, as in the case of NO_3^{--} . The small g values can be explained if the next unoccupied energy levels and the odd electron level have the same symmetry and allow a mixing of the electron state with higher levels. However,

TABLE II. Paramagnetic centers in KBr. $A/g_e\beta_e$, $B/g_e\beta_e$, $C/g_e\beta_e$, and W in gauss; the brackets indicate the crystallographic orientation of the principal tensor axes.

No.	Center	$T(^{\circ}\text{C})$	g_z	g_x	g_y	$A/g_e\beta_e$	$B/g_e\beta_e$	$C/g_e\beta_e$	W
1	NO int.	-100	2.0037 ± 0.0002 [100]	2.0089 ± 0.0002		32.3 ± 0.5 [100]	5.7 ± 0.4		2.0 ± 0.5
2	NO+[+]	-100		2.0072 ± 0.0004			14.2 ± 0.4		3.0 ± 0.3
3	$\text{NO}_3^{--}+[-]$	-190	2.0020 ± 0.0006 [111]	2.0068 ± 0.0006		65 ± 1 [111]	32 ± 1		20 ± 2
		0		2.0042 ± 0.0003			40.3 ± 0.5		10 ± 1
4	$\text{NO}_2^{--}+[-]$	-190	2.0015 ± 0.0020 [110]	2.0003 ± 0.0020		43 ± 5 [110]	62 ± 5		6.5 ± 0.7
5	$\text{O}_2^{+}+[+]$	-190	2.0418 ± 0.0003 [100]	2.0035 ± 0.0003 [011]	2.0103 ± 0.0003 [011]	0	0	0	3.2 ± 0.4

the behavior of the g tensor is difficult to explain, and we cannot propose any model thus far.

D. Oxygen in KCl

The last center of Table I (Fig. 5) is the only one that does not show any hfs, indicating its connection with a reaction product involving no nitrogen. It can be observed below -100°C , but only in crystals doped in the melt. It is probably also present in doped powders, but the spectrum is then smeared out. It never occurs in crystals heated in NO or NO_2 gas and irradiated with x or γ rays for less than one hour. The behavior during electron or hole release in the crystal shows that it is produced by hole trapping. If a crystal doped in the melt or in the gas is irradiated at room temperature for a long time (1 week), the EPR signal increases by a factor of 10. As the centers are anisotropic, they are not due to atomic oxygen ions which have room to rotate as well in the interstitial sites as in the vacancies. They involve neither oxygen bound to chlorine nor potassium, because the spectrum would then show a multiplet instead of a singlet. O_2^- has to be ruled out as it has different magnetic parameters.¹¹ A possible model is an O_2 molecule, losing an electron during irradiation to become an O_2^+ molecule ion; it then has the tendency to neutralize a neighboring chlorine ion, but if it is located in a positive-ion vacancy it is stabilized by the Madelung field. In another model, all the oxygen in the crystal is in the form of O_2^- molecule ions, which are present in large

quantity according to Känzig and Cohen¹¹; they lose an electron during irradiation, and give neutral oxygen molecules with a spin of one, observable by EPR.

In crystals doped in the melt, the nitrate and nitrite decompose thermally, releasing oxygen that diffuses and recombines in the vacancies; in crystals heated in the gas and containing only NO, such a dissociation should not occur unless it is produced by x or γ irradiation. This would explain the large increase of the spectrum intensity after a long exposure to gamma rays.

E. Centers in KBr and KI

In potassium bromide and iodide, we find the same paramagnetic species (Tables II and III), but in different concentrations, and the lines are generally broader, because of the larger magnetic moment of the halide nuclei. The determination of the magnetic parameters is thus less accurate.

The nitric oxide and the NO_3^{--} ions are present in both halides, but the relative concentration of the latter is greatly enhanced in KBr and even more in KI with respect to KCl; in potassium iodide, the lines of the low-temperature spectrum are so broad that they cannot be resolved and measured unless the magnetic field is parallel to [100], where they coincide; the g factors and hfs can be estimated to be about the same as in KBr.

Whereas the stability of interstitial nitric oxide is maintained in KBr, its resonance in KI can be observed only if the crystal is irradiated and kept at liquid nitro-

TABLE III. Paramagnetic centers in KI. $A/g_e\beta_e$, $B/g_e\beta_e$, $C/g_e\beta_e$, and W in gauss; the brackets indicate the crystallographic orientation of the principal tensor axes.

No.	Center	$T(^{\circ}\text{C})$	g_z	g_x	g_y	$A/g_e\beta_e$	$B/g_e\beta_e$	$C/g_e\beta_e$	W
1	NO int.	-190	2.0037 ± 0.0003 [100]		2.0113 ± 0.0003	37.0 ± 0.2 [100]		3.8 ± 1.5	10 ± 1
2	NO+[+]	-100		2.0084 ± 0.0003			14.2 ± 0.6		3.3 ± 0.3
3	$\text{NO}_3^{--}+[-]$	-190	[111]	2.0050 ± 0.0006 2.0050 ± 0.0006		[111]	46 ± 1 44 ± 1		30 ± 10 15 ± 2

¹¹ W. Känzig and M. H. Cohen, Phys. Rev. Letters 3, 509 (1959).

gen temperature; heating up to -140°C for 5 min decreases the EPR signal to about $\frac{1}{2}$.

NO_2^{--} is absent in KI; this is consistent with the infrared spectrum that shows in the measured crystal a $\text{NO}_2^-/\text{NO}_3^-$ concentration ratio at least 20 times smaller than in the other halides. It occurs in KBr heated in NO gas (in opposition to KCl), its signal there being more intense than those of nitric oxide.

Oxygen molecules are present in a small concentration in KBr irradiated for a long time, but are undetectable in KI.

The sequence KCl-KBr-KI shows an increase in the average oxidation state of the nitrogen, with a corresponding decrease in free oxygen; although this could be due to the lowering of the melting point, as suggested by Maslakowez,¹ it seems to be rather a property of the solid lattice too, as the shift in the equilibrium is also observed in the crystals heated in the gas at the same temperature.

F. Unidentified Centers

In KCl and KBr, two other centers have been observed, with the parameters:

Center 6, $g=2.0052\pm0.0002$, $A=12.0\pm0.2$ gauss;

Center 7, $g=2.0062\pm0.0002$, $A=21.8\pm0.2$ gauss.

They are isotropic at all temperatures down to -190°C ; their behavior during optical electron or hole release indicates that the former is produced by electron and the latter by hole trapping. If KCl crystals are heated to 100°C for 10 min, all the signals disappear, except center 7 which increases; on the other hand, if the crystal is exposed to ultraviolet light, all the centers are bleached but center 6, which doubles its signal intensity before it decreases slowly. In crystals heated in NO gas, 7 is present in a relatively large concentration in KBr, but not in KCl, with an inverse distribution in crystals doped from the melt.

The hyperfine splitting is much smaller than has been previously measured for NO_2 (47 gauss in the gas,¹² 58 gauss in an argon matrix,¹³ 107 gauss in a solution of CCl_4 ¹⁴), so that it is improbable that nitrogen dioxide trapped in vacancies produces the observed signals. Without more extensive experimental information, we cannot answer the question of their identity.

¹² J. G. Castle and R. Beringer, Phys. Rev. **80**, 114 (1950) (L).

¹³ C. K. Jen, S. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **112**, 1169 (1958).

¹⁴ G. R. Bird, J. C. Baird, and R. B. Williams, J. Chem. Phys. **28**, 738 (1958).

IV. CONCLUSION

With selective doping processes combined with optical and thermal release of free electrons and holes from the host-lattice imperfections (F centers and Cl_2^-), it has been possible to suggest the following models for the observed centers. In all the examined halides, the nitric oxide enters either from the melt as a dissociation product, or from the gas phase when the partial pressure is high enough; it is included in the lattice as nitrosyl halide, which dissociates under irradiation, giving nitric oxide, rotating freely in positive-ion vacancies or locked in interstitial sites in $[100]$ orientation. The nitrate ions, in negative-ion vacancies, become doubly charged during irradiation and are immobilized electrostatically at low temperatures in (111) planes. In KCl and KBr the same occurs to nitrite ions, but they are locked in $[110]$ orientations. The linewidths range from 1 to 12 gauss in KCl, but are roughly doubled in KBr and tripled in KI. At high temperature, the different compounds react with each other to attain equilibrium concentrations that are dependent on the host crystal and of the gas mixture around it.

The interpretations of the EPR spectra take into account only simple experimental facts; their validity has to be verified by more refined theoretical calculations for the proposed models. Another way to obtain more detailed information on the centers is to examine their optical properties in comparing the absorption of the samples with their EPR spectra; this is a difficult investigation because of the low intensity and the overlap of the absorption lines, as our preliminary measurements have shown. A search for analogous species in other doped alkali halides will certainly allow interesting comparisons. In addition, measurements performed at lower temperatures down to liquid helium are necessary to identify the last-mentioned isotropic centers.

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