tion to the thermoelectric power due to electron-phonon interaction is proportional to $l_\phi'/l_{e\phi}$;[3] the numerator l_ϕ' represents the mean free path of those phonons which interact with electrons, while $l_{e\phi}$ is the free carrier mean free path determined by collisions with phonons. From the mobilities one calculates that $l_{e\phi}$ at 150°K is 5×10^{-6} cm for holes and 6×10^{-5} cm for electrons. The average mean free path of all the phonons can be evaluated from thermal conductivity data[8]; assuming that the mean free path for long wavelength phonons is about 10 times larger, one finds for l_ϕ' a value of 10^{-5} to 10^{-4} cm. Calculation then shows that the phonon-hole interaction yields already a measurable contribution to the thermoelectric power at 150°K, while that due to the phonon-electron interaction is quite negligible.

Note added in proof.—The values for the effective masses have been calculated taking the proper correction for impurity scattering into account.

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Electron Spin Resonance of V_1-Centers*

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THE electron spin resonance of the F-center (electron bound to a negative ion vacancy) has been investigated extensively in the past.[1] The hyperfine splitting has not been resolved. This suggests that the electron interacts with the magnetic moments of many nuclei and consequently that its wave function is distributed over many ions near the vacancy. The present work indicates that the electronic structure of the supposed antimorph of the F-center, the V_1-center (hole bound to a positive ion vacancy[2]), is entirely different. A large resolvable hyperfine splitting has been observed in the V_1-center resonance. The pattern per-

TABLE I. g-factors of the different families in the KCl spectra. Limit of error ±0.001. The calculated g-factors are based on $g_\perp = 2.042$ and $g_{||} = 2.0023$.

Field direction	$\theta = 45°$, 35° and 60° Exp.	Calc.	θ	$\theta = 90°$ Exp.	$\theta = 0°$ Exp.	
(100)	2.024	2.022	45°	2.042	...	...
(111)	2.015	2.015	35°	2.042 $\}g_\perp$	...	...
(110)	2.032	2.032	60°	2.042	2.002	$g_{||}$

TABLE II. Average spacing in gauss between the groups in the different families of the KCl spectra. Limit of error ±0.5 gauss.

Field direction	$\theta = 45°$, 35°, and 60°	θ	$\theta = 90°$	$\theta = 0°$
(100)	69.6	45°	10.5	...
(111)	83.0	35°	10.0	...
(110)	54.2	60°	10.0	102.0

mits a detailed analysis of the electronic structure of this center and we have concluded that the hole is localized on but two negative ions.

KCl, NaCl, KBr, and LiF single crystals were placed in a resonant cavity and irradiated with x-rays at −180°C. Then, without warming the crystal, we investigated the magnetic resonance spectrum with a high sensitivity resonance spectrometer operating at about 9300 Mc/sec. A modulation of the dc magnetic field of 0.1 to 1.0 gauss was used. The crystals were then warmed to a selected temperature and cooled again to −180°C. Upon remeasurement of the spectrum it was found that all lines had faded in the same proportion. This indicates that every spectrum is essentially due to a single kind of trap. The temperature region in which fast fading occurs coincides in the case of KCl and KBr with the temperature region in which the V_1-band bleaches.[3] In NaCl, fast fading occurs between −140°C and −120°C, in LiF between −160°C and −140°C. No optical data are available for these two substances.

The resonance spectra depend very sensitively upon the orientation of the crystals in the magnetic field. The cases $H||(100)$, $H||(111)$ and $H||(110)$ have been investigated. In the case of KCl the spectra can be decomposed into families of lines, each family consisting of seven almost equally spaced groups. The integrated intensity ratio of the groups is 1:2:3:4:3:2:1. The number of families is 2 for $H||(100)$ and $H||(111)$, and 3 for $H||(110)$. The g-factors corresponding to the center lines of the families are larger than the free-electron value except in the case of one of the families in the $H||(110)$ pattern, for which g is equal to the free-electron value within experimental error. As the nuclear spin of Cl is $\frac{3}{2}$, the number of the groups (7) and their intensity ratio indicates that the hole spends its time near two halogens only, i.e., the V_1-center is essentially a Cl_2^- molecule-ion which is presumably near a positive-ion vacancy. The observed splitting agrees satisfactorily with the theoretical splitting calculated under the assumption of dipolar interaction by using Sternheimer's[4] $\langle 1/r^3 \rangle$ values of the halogen p-functions. The g-shifts as well as the splittings can be explained quantitatively if we assume axially symmetric Cl_2^- molecule-ions oriented in the (110) directions. The distribution over the six different (110) directions is statistical. Tables I and II show as an example the main resonance data for KCl.

TABLE III. Approximate line width in gauss.

| | KCl | | | | | |
	Cl³⁵−Cl³⁵	Cl³⁵−Cl³⁷	Cl³⁷−Cl³⁷	NaCl	KBr	LiF
Line width in gauss	2.4	2.0	1.6	7.5	4	17

The variation of the splitting with the angle θ between the bond direction and the magnetic field enables us to determine the admixture of s and p functions on the halogens. We have obtained 30% s and 70% p for both KCl and NaCl. For $|\psi(0)|^2$, we have obtained 1.9×10^{24} cm⁻³.

The KBr spectra are more difficult to analyze because of second-order effects and quadrupole effects. However, the analysis indicates the existence of Br_2^- molecule-ions. Second-order effects play also an important part in LiF. A tentative analysis suggests that the bond direction of the F_2^- molecule-ion is (110).

Typical values of the observed line widths are listed in Table III. It appears that the predominant relaxation is due to hyperfine interaction. Spin-spin interaction seems also to play a role, and this indicates that high local concentrations of color centers might be formed by x-irradiation.

A full account of the present investigations will be published in a forthcoming paper. The analysis of the results was only possible through the advice of C. P. Slichter and the continuous help of T. G. Castner.

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Effect of Proton Irradiation upon the Electrode Potential of Tungsten

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NUCLEAR irradiation may be expected to alter the electrochemical and chemical properties of metals. As a preliminary study we have measured the effect of proton irradiation upon the electrode potential of tungsten in aqueous salt solutions. Tungsten wire specimens 0.012 in. in diameter were chosen since previous investigations[1] have shown that at room temperature the radiation effects in this material are quite stable. Reproducible and steady electrode potential measurements were obtained by means of the following procedure. The tungsten surfaces were degreased with alcohol and acetone, immersed in a strong aqueous solution of ammonia for several minutes, and washed with an oxygen-free saturated solution of KCl in dis-

tilled water. The specimens were then placed in an oxygen-free saturated solution of KCl in distilled water, and their electrode potentials were measured against a saturated calomel cell with a vacuum-tube potentiometer. The solution and the standard cell were kept at 30°C in a thermostat. The results obtained are shown in Table I.

First of all it should be pointed out that after bombardment the wires were very slightly radioactive (about 1000 counts per minute), presumably because of some minor impurities. This activity is much too weak to produce any significant changes in the electrolyte and thus the observed effects have to be ascribed to radiation-induced changes in the metal. It appears that the effect of proton irradiation upon the electrode potential of tungsten is large and actually it is much greater than the effect of severe cold work. At first glance the magnitude of the observed effect is surprising in view of the fact that the diameter of the wire is less than one percent of the mean free path of the 260-Mev proton in tungsten. It should be remembered, however, that the majority of the radiation effects produced under these conditions appears to be caused by highly effective secondary nucleons produced in inelastic collisions rather than by elastic collisions of the incident protons.[1] The results indicate also that the change in electrode potential increases with the intensity of the proton beam as expected. The greater change obtained with protons of 130-Mev energy than with 260-Mev protons is rather difficult to understand and may not be real. In all cases the potentials of the irradiated specimens are anodic (less noble) to the annealed specimens, which means that irradiation makes the tungsten more reactive chemically.

The experiments show that irradiation alters significantly the electrochemical properties of metals, and that such measurements may be used to study the nature and extent of the effects produced. One would expect the change of the electrode potential to be associated with production of localized lattice imperfections at the metallic surface. These defects are primarily dislocations formed either by displacement spikes or by collapse of vacancy clusters. Other defects such as vacancies and interstitials, even if they were sufficiently stable in the interior of the grains, would probably disappear rather rapidly near the surface. The

TABLE I. Electrode potentials of proton irradiated tungsten.

Treatment	Proton irradiation	Electrode potential[a] millivolts (anodic)
Annealed[b]	none	0
Cold drawn	none	22
Annealed and irradiated	1.9×10^{15}/cm² at 130 Mev	72?
Annealed and irradiated	1.8×10^{15}/cm² at 260 Mev	39
Annealed and irradiated	6.8×10^{15}/cm² at 260 Mev	47
Annealed and irradiated	2.2×10^{16}/cm² at 260 Mev	84
Irradiated and annealed[b]	2.2×10^{16}/cm² at 260 Mev	0

[a] The electrode potentials are reported *versus* the annealed tungsten.
[b] The annealed specimens were heated for 2 hours at 900°C in an argon atmosphere.