

Monovalent Samarium in Potassium Chloride*

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Potassium chloride crystals have been doped with Sm^{2+} ions to concentrations of $5 \times 10^{19} \text{ cm}^{-3}$, resulting in identifiable Sm^{2+} absorption spectra. Heating of the doped crystals in K vapor produces no visible change in the samples. Exposure to gamma irradiation at room temperature leads to a decrease in the Sm^{2+} absorption bands accompanied by an equivalent growth in the near infrared of a characteristic spectrum which can be explained in terms of electric dipole transitions between the $4f^6 6s^1$ and $4f^5 6s^2$ configurations of the Sm^{1+} ion. The conclusion that Sm^{2+} ions are reduced to Sm^{1+} by the capture of an electron is supported by the observation that the growth rate of the Sm^{1+} bands is equal to the decay rate of the Sm^{2+} bands. Magnetic susceptibility and electron paramagnetic resonance (EPR) observations are shown to be consistent with the reduction hypothesis.

I. INTRODUCTION

THE lanthanides may be ionized by the successive removal of electrons. With the exception of lutetium, the first stage of ionization results from the removal of a $6s$ electron. The second stage of ionization involves the removal of the other $6s$ electron. At the third stage, both the $6s$ electrons and a $5d$ or a $4f$ electron have been removed to leave, apart from the xenon structure, a $4f^n$ configuration, where $n=1$ for cerium and increases regularly to $n=14$ for lutetium. Although the tripositive oxidation state is commonly known to dominate throughout the lanthanide series, several techniques have been developed in recent years for the stabilization of the divalent state in dipositive alkaline-earth halides.¹ In view of this, it might be expected that Sm^{2+} ions in KCl could similarly be reduced to the monovalent state.

In the present work, the reduction of divalent samarium ions in potassium halides to the monovalent state is investigated in a semiquantitative manner. The usual absorption due to Z centers in the case of divalent alkaline-earth-doped alkali halides has not been observed. Instead, an absorption spectrum consistent with the $4f^6 6s^1 \rightarrow 4f^5 6s^2$ absorption of Sm^{1+} ions was observed. We believe that these studies represent the first observation of a lanthanide in the monovalent state which is stable in its environment at low temperatures.

The kinetics of the conversion process, the optical as well as the magnetic properties of the single-ionized samarium ions will be discussed in the following sections.

II. EXPERIMENTAL PROCEDURE

Optical-grade KCl containing varying quantities of SmCl_3 (0.5–2.0 mole %) was purified under an atmos-

* A preliminary account of this work has been reported in the September meeting of the American Physical Society in Honolulu, 1965. *Bull. Am. Phys. Soc.* **10**, 686 (1965).

¹ F. K. Fong, *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon Press, Inc., New York, 1966), Vol. III, Chap. 4.

phere of HCl at 500°C . Single crystals were then grown from the melt by the Czochralski method at a pulling rate of 0.21 mm/min under a continuous flow of dried H_2 . Concentrations of Sm in the resulting crystals were then determined quantitatively both by ethylenediamine tetra-acetic acid (EDTA) analysis and a spectrophotometric technique. The specimens contained, respectively, 0.02, 0.087, 0.22, and 0.32 mole % Sm.

Absorption spectra were made with Cary 14R and Beckman DK2 spectrophotometers at cryogenic temperatures (77 and 4.2°K) to achieve maximum resolution of absorption bands and to insure the stability of gamma-irradiated samples. Gamma irradiation was achieved at room temperature with a Co^{60} source at an approximate rate of 10^6 rad h^{-1} . Between measurements, the irradiated samples were stored in the dark at dry-ice temperature. The additive treatment with K vapor was made according to the procedure previously described.²

Paramagnetic-resonance measurements were made at 77 and 4.2°K with 9000 Mc/sec and a 4-in. Geneva magnet up to a field strength of 7300 G. Magnetic-susceptibility measurements were made in the temperature range $2.3\text{--}310^\circ\text{K}$ using the Faraday method in an average field of $\approx 15 \text{ kG}$.

III. EXPERIMENTAL RESULTS

The samples employed in the present study contained 0.02, 0.087, 0.22, and 0.32 mole % (see Sec. II) corresponding to Sm-ion concentrations of 3.2×10^{18} , 1.4×10^{19} , 3.5×10^{19} , and $5.1 \times 10^{19} \text{ cm}^{-3}$, respectively. The experimental results pertinent to our discussion may be summarized in categories as follows.

(1) Figures 1 and 2 show a typical group of spectra for one sample subjected to successively longer gamma-irradiation times. The visible spectral region is shown

² J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

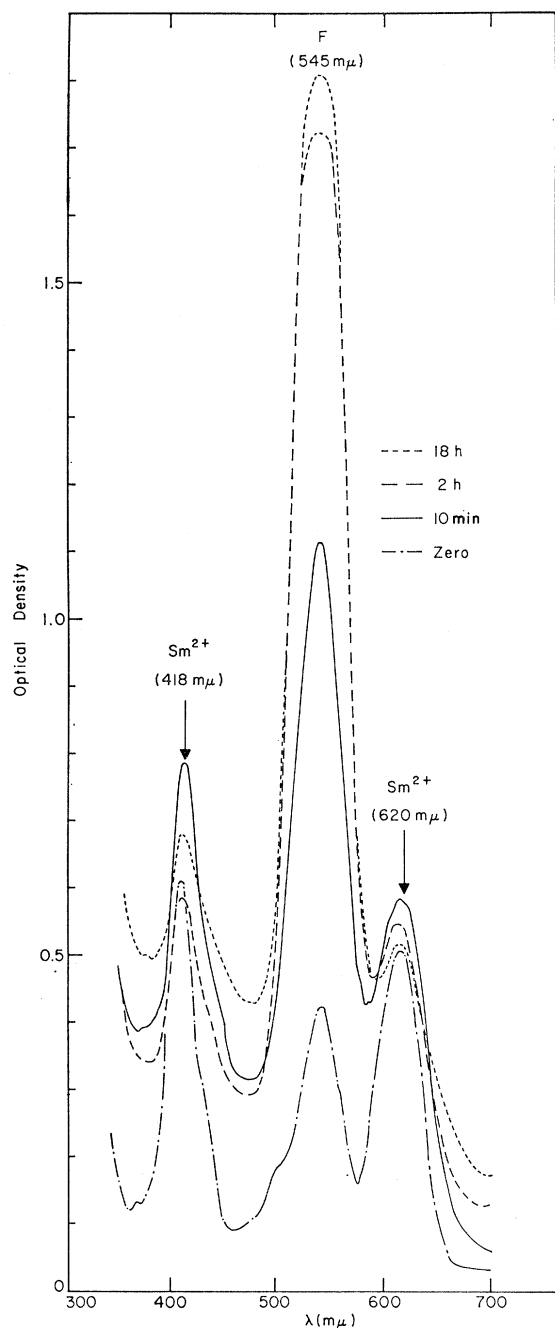


FIG. 1. Absorption of KCl:Sm in the visible range of the spectrum showing the effects of gamma irradiation. The sample contains 1.4×10^{19} Sm^{2+} ions/ cm^3 . While the F band grows with irradiation, the Sm^{2+} bands actually diminish. The spectra were measured at 77°K with sample thickness = 0.077 cm.

in Fig. 1, and the weaker near-infrared spectra of a thicker sample of the same dopant concentration are shown in Fig. 2. The salient features shown appear to be: (a) No Sm^{3+} $4f-4f$ absorption bands are evident throughout the entire spectral range investigated, indicating that Sm ions do not exist in the trivalent

state in KCl; (b) A rapid growth (particularly at the beginning) occurs for the F ($545 \text{ m}\mu$) and M ($805 \text{ m}\mu$) bands with the subsequent appearance at longer times of the R band ($726 \text{ m}\mu$); (c) The Sm^{2+} bands decrease with irradiation time, as evidenced by the bands at 418 and $620 \text{ m}\mu$; (d) The emergence of a weak, but characteristically identifiable absorption spectrum in the near infrared (Fig. 2) with absorption maxima at 861 , 962 , 1119 , and $1250 \text{ m}\mu$. The detailed dependence on irradiation time of the principal absorption bands is shown on Fig. 3.

(2) Thermal bleaching occurs rapidly when the sample is heated up to 150°C . Bleaching is accompanied by thermoluminescence, which corresponds to the fluorescence of Sm^{2+} ions. After warming to 150°C , the sample is rapidly reverted to the original (unirradiated) state, as is shown by the absorption spectra (Fig. 4).

(3) After the specimens have been subjected to 2 h. of gamma irradiation at room temperature, a density of approximately $(1.5-1.7) \times 10^{17}$ F centers/ cm^3 is observed apparently independent of the Sm^{2+} concentration. In all cases, the Sm^{2+} bands diminish with time of irradiation.

(4) Specimens containing 3.5 and 5.1×10^{19} Sm ions/ cm^3 were heated in distilled K vapor simultaneously with samples of pure KCl at 650°C for 24 h. and subsequently quenched. The pure KCl samples were additively colored with a density of 1.5×10^{17} F centers/ cm^3 .³ No additive coloration, however, was observed in the Sm^{2+} -doped samples.

(5) The paramagnetic resonance spectrum of an irradiated sample containing 5.1×10^{19} Sm ions/ cm^3 at 77°K shows a weak resonance of half-width 41 G at g slightly higher than 2, while a similarly irradiated sample with a density of 3×10^{17} F centers/ cm^3 gave no

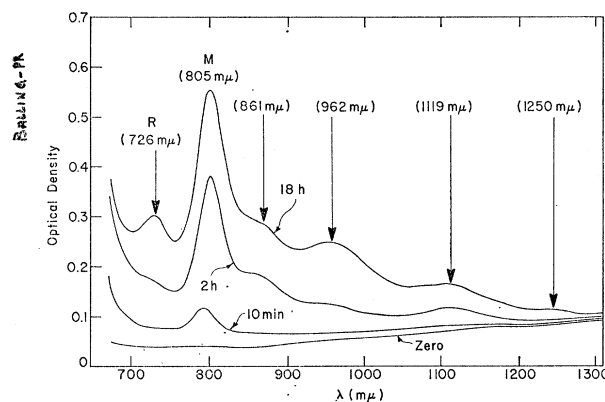
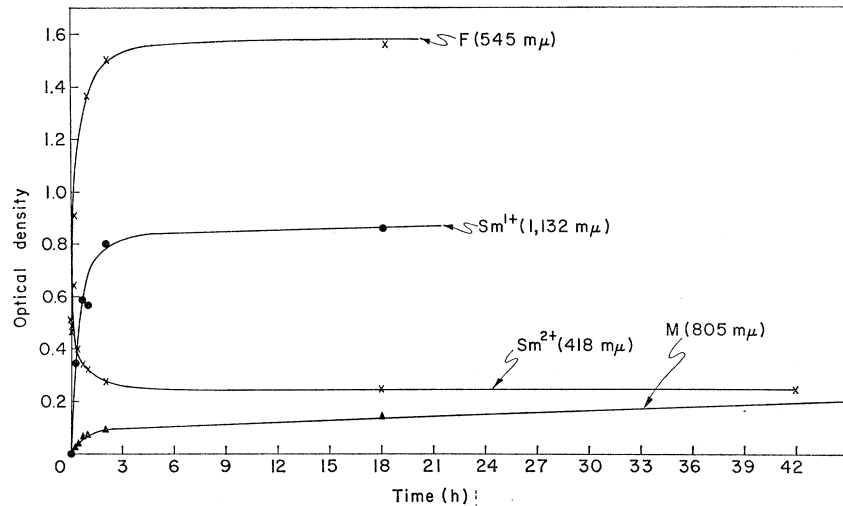


FIG. 2. Near-infrared part of the KCl:Sm absorption. Same remarks apply as in Fig. 1, except that the sample in this case is thicker (0.14 cm) to show more clearly the considerably weaker absorption. Bands to the long-wave side of the M band have been identified as belonging to Sm^{3+} ions (see text).

³ The concentration of F centers is estimated from the height and half-width of the F band by employing Smakula's equation. See, for example, Ref. 2, Chap. III.

FIG. 3. Plot of the optical density at band maximum versus irradiation time for the principal bands of Figs. 1 and 2. Note that the F , M , and Sm^{1+} bands grow while the Sm^{2+} band decays.



signal under identical conditions. The signal vanishes upon warming of the sample and no resonance was observed in the case of samples with lower Sm concentrations. No hyperfine structure has been resolved.

(6) The volume susceptibility of KCl doped with 5.1×10^{19} Sm^{2+} ions/ cm^3 was measured before and after 2 h of gamma irradiation. In Fig. 5 are shown the data after subtraction of the weak diamagnetic susceptibility of KCl. The two curves can be represented with good accuracy at low temperatures by the expressions

$$\chi_{\text{before}} - \chi_{\text{KCl}} = 7.4 \times 10^{-7} + 1.1 \times 10^{-6}/T, \quad (1)$$

$$\chi_{\text{after}} - \chi_{\text{KCl}} = 5.7 \times 10^{-7} + 1.7 \times 10^{-6}/T. \quad (2)$$

IV. THE MONOVALENT STATE OF SAMARIUM IN POTASSIUM CHLORIDE

The free Sm^{1+} ion has a $4f^6 6s^1$ ground configuration^{4,5} for which the ground term $^8F_{1/2}$ has been assigned according to the LS coupling scheme. In the following, however, we assume a jj coupling of the $6s$ electron to the $4f^6$ configuration, because the resulting $(^7F_0, \frac{1}{2}, \frac{1}{2})$ ground state appears to give better agreement with magnetic data. The six $4f$ electrons will be coupled according to the LS coupling scheme with 7F_0 as the ground J level. The remaining $6s$ electron with $j = \frac{1}{2}$ will be coupled to the 7F_0 level through a jj coupling, giving an S state with a total angular momentum of $J = \frac{1}{2}$. If the crystal field is taken into account, the ground level $(^7F_0, \frac{1}{2}, \frac{1}{2})$ will transform according to the Γ_1 representation of the cubic symmetry.

A. Optical Properties of Sm^{1+} Ions

Since impurity cations enter alkali halides substitutionally, the Sm^{1+} ion is expected to be in a cubic

site, and parity is a good quantum number. Electric dipole transitions are therefore forbidden within the ground configuration, except perhaps through the mixing of vibronic transitions that involve an odd vibrational mode of the lattice. Such transitions, however, may be expected to be rather weak because trivalent rare-earth ions give no vibronic transitions at low concentrations in ionic-crystal hosts. If the transitions corresponding to the spectrum which emerges as the Sm^{2+} bands diminish [see result (1), (c), (d) and Fig. 2] are optical transitions of the Sm^{1+} ion, they must involve an excited configuration with odd parity, such as $4f^6 6s^2$. At first sight, it may be expected that this configuration should give rather low intensity owing to

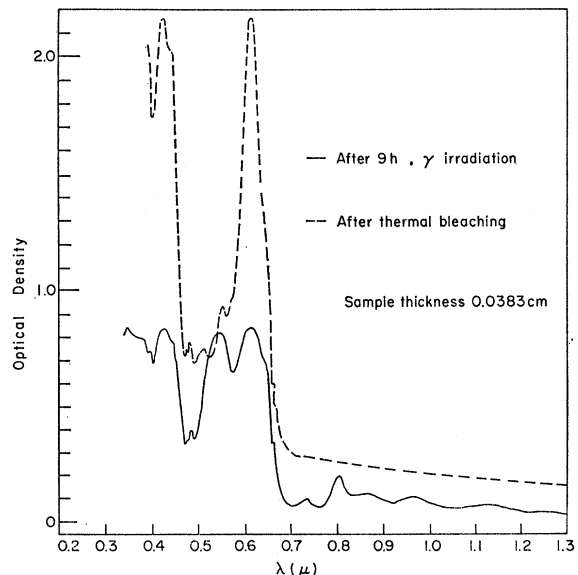


FIG. 4. Thermal bleaching of the absorption bands formed by gamma irradiation. After warming to 150°C , the spectrum has reverted to its initial state before irradiation. Note the Sm^{2+} bands at 418 and 620 $m\mu$, and the F band at 545 $m\mu$.

⁴ M. A. El'Yashevich, U. S. Atomic Energy Commission Office of Technical Information, Translation Series, AEC-tr-4403, 1953 (unpublished).

⁵ W. Albertson, Phys. Rev. 49, 209 (1936).

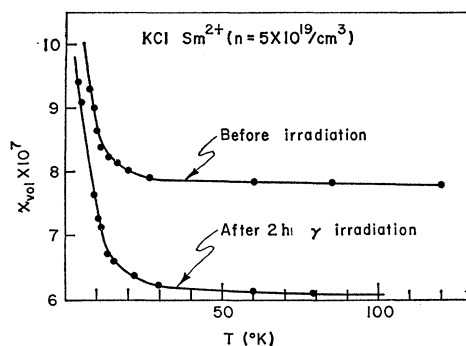


FIG. 5. Paramagnetic susceptibility before and after gamma irradiation of KCl-Sm (corrected for the diamagnetism of pure KCl) versus temperature. Data were taken by the Faraday method in an average field of ≈ 15 kG and are for samples containing 5.1×10^{19} Sm ions/cm 3 .

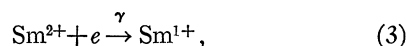
the $\Delta l=3$ transitions. The $6s$ configuration, however, must be mixed with other configurations to a large extent because of interaction with the ligands. The quantum number s will lose its meaning, and the Δl selection rule will be accordingly weakened.

If we neglect the closed shell $6s^2$, the configuration $4f^5 6s^2$ appears the same as the configuration $4f^5$ with the ground term 6H . Spin-orbit interaction in the $4f^5 6s^2$ configuration is expected to be very similar to that in the $4f^5$ configuration in Sm^{3+} since the two additional $6s$ electrons have very little effect near the nucleus and since the spin-orbit interaction has a dependence of $1/Z^4$, where $Z=62$ in both cases.

In Fig. 6, the proposed Sm^{1+} bands are compared with an energy-level diagram of the 6H term of Sm^{3+} .⁶ The agreement is excellent with only one J level ($J=13/2$) unidentified, which is most likely hidden under the strong M -center band at $12\,514\text{ cm}^{-1}$. The above interpretation should be valid regardless of the coupling scheme of the ground $4f^6 6s^1$ configuration.

B. Kinetic Consideration of the Electron-Capture Process: $\text{Sm}^{2+} + e \rightarrow \text{Sm}^{1+}$

Following the argument of the preceding paragraphs, one may represent the gamma-ray destruction of Sm^{2+} by the electron-capture process



where the symbol γ denotes the assumption that the electrons are produced by the gamma rays from elemental ionization processes independent of the Sm^{2+} concentration. Thus, one expects that the rate of conversion of Sm^{2+} by electron capture will be given by

$$dn_2/dt = -n_2/\tau, \quad (4)$$

where n_2 is the concentration of Sm^{2+} ions, and the

⁶ G. H. Dieke, *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 170.

lifetime τ is of the form $1/\tau = \sigma n_e v_e$. Thus, the decay rate of Sm^{2+} is proportional to the concentration of traps n_2 , the trap cross section for electron capture σ , and the average thermal current of the electrons $n_e v_e$, n_e and v_e being the concentration and thermal velocity of the conduction electrons, respectively.

In Eq. (3), we have tacitly assumed that the Sm^{2+} ions that capture electrons end up in the monovalent state. If we further assume that there are no processes competing with (3), i.e., that $n_1 + n_2 = n_0$ (n_1 and n_0 being the Sm^{1+} and initial Sm^{2+} ion concentrations, respectively), then we have

$$dn_1/dt = -dn_2/dt. \quad (5)$$

Equations (4) and (5) integrate to the familiar exponential rate equations

$$n_2 = n_0 e^{-t/\tau}, \quad n_1 = n_0 (1 - e^{-t/\tau}). \quad (6)$$

Since the optical density of an absorption band is proportional to the concentration of absorbers according to the Beer's law, the same time dependence as in (6) should be observed in the heights of principal absorption bands corresponding to Sm^{2+} and Sm^{1+} ions. In Fig. 7, we have compared the growth rate of the $1.119\text{ }\mu$ band of the Sm^{1+} spectrum with the decay rate of the $412\text{-m}\mu$ Sm^{2+} band. It will be seen that the slopes ($1/\tau = 3.09 \times 10^{-4}\text{ sec}^{-1}$) for both the growth and decay plots for the two respective bands are essentially identical within experimental error, in agreement with our hypothesis. For purpose of comparison, Fig. 7 also shows the growth of F centers corresponding to the capture of electrons by Cl^- vacancies. It is to be noted that F centers are produced at a substantially greater rate ($1/\tau = 1.09 \times 10^{-3}\text{ sec}^{-1}$) than Sm^{1+} ions.

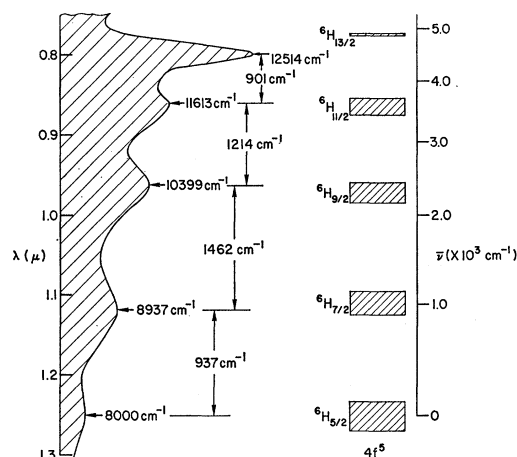


FIG. 6. This illustrates how the observed Sm^{1+} spectrum at 4.2°K is explained by assuming an energy-level structure similar to that of the ground 6H term of Sm^{3+} . Note that the observed separations are in excellent agreement with the 6H splittings (see text).

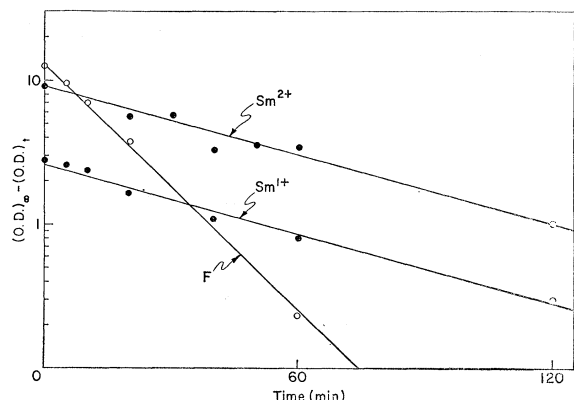


FIG. 7. The data of Fig. 3 plotted on a logarithmic scale as a function of irradiation time. The vertical axis actually represents $\log[\pm(O.D.)_0 \mp (O.D.)_t]$ in the case of Sm^{2+} and Sm^{1+} , respectively. (O.D. = optical density.) From Eq. (6), the slopes of these plots give the quantity $1/\tau$. The important result is that the Sm^{1+} band grows at the same rate as the Sm^{2+} band decays. The much faster growth rate of the F band is also shown.

C. Magnetic Properties of the Sm^{1+} Ions

The electron paramagnetic resonance (EPR) spectrum observed in the gamma-irradiated KCl sample containing 5.1×10^{19} Sm ions/cm³ [result (5)] is believed to be due to Sm^{1+} ions. At g slightly greater than two, a weak signal was observed in the gamma-irradiated Sm-doped sample, whereas a sample not containing Sm but subjected to a similar irradiation schedule showed no detectable resonance. The observed spectrum had no hyperfine structure, and was difficult to reproduce regularly, in part because of a low signal-to-noise ratio, and probably, in part, because of the thermal instability of the Sm^{1+} ions. That the observed signal is not due to F centers is established by the fact that no signal has been detected in the undoped sample which contained approximately 5×10^{17} F centers/cm³, while the concentration of F centers in the gamma-irradiated Sm-doped samples was 1.5×10^{17} /cm³ [result (4)]. The observed resonance is consistent with the $4f^6 6s^1$ configuration of the Sm^{1+} ion as described above. For an s -type ground state, the resonance is expected to be at $g=2$.⁷

The ions Sm^{2+} and Eu^{3+} are isoelectronic, and have the same $4f^6$ configurations. The ground state 7F_0 is nonmagnetic, and any contribution to paramagnetic susceptibility results from the mixing of 7F_1 excited state with the ground state 7F_0 . One might therefore expect that the magnetic susceptibility of the Sm^{2+} -

⁷ For free-ion Sm^{1+} , Albertson⁵ observed $g=4.32$.

doped crystal should be nearly equal to that of a similar crystal doped with Eu^{3+} ions in equal concentration. The latter case is described by Van Vleck⁸ and one calculates for the volume susceptibility for a concentration of 5.1×10^{19} /cm³ at $T \lesssim 50^\circ\text{K}$ $\chi_{\text{calc}} = 7.3 \times 10^{-7}$, in excellent agreement with the first term on the right side of Eq. (1). Thus if this term is to be associated with the Sm^{2+} ions, the value of 5.7×10^{17} in (2) suggests that about 20% of the Sm^{2+} ions have been reduced by the gamma irradiation. This result is in fair agreement with the optical data.

On the other hand, the behavior of the Curie terms is not as easily explained. While the weak Curie term in the nonirradiated sample is not surprising (possibly due to the presence of paramagnetic impurities, or F centers in concentrations of $\sim 10^{17}$ to 10^{18} , or even to the temperature dependence of Sm^{2+} not accounted for), the Curie constant in (2) appears to be too small. If the $4f^6 6s^1$ configuration of the Sm^{1+} ion (as discussed in Sec. IIIA.) corresponds to $J = \frac{1}{2}$ and $g = 2$, for a concentration of 10^{19} Sm^{1+} cm⁻³ one would calculate the Curie constant $C \approx 6 \times 10^{-6}$, which is roughly three times greater than that observed.

V. SUMMARY

In the above sections we have presented evidence that the Sm^{2+} ions incorporated in KCl crystals are reduced to the monovalent state by gamma irradiation at room temperature. The Sm^{1+} ions evidently exhibit electric dipole transitions between the even $4f^6 6s^1$ configuration and the odd $4f^5 6s^2$ configuration. The Sm^{1+} ions are thermally unstable and readily revert to the divalent state with emission characteristic of the Sm^{2+} ions.

Much is left for future investigations. The observed EPR spectrum [result (5), Sec. III], for example, showed no sign of an expected hyperfine structure. This can probably be resolved by the ENDOR technique. Low-temperature gamma-irradiation experiments should prove to be informative, as should also extension to lanthanide impurities other than Sm^{2+} ions.

ACKNOWLEDGMENT

We are grateful to J. Mohl for the growth of single crystals, to P. Romo for the EDTA analysis of the Sm content in various samples, and to F. Krajenbrink and D. Leslie for their technical assistance.

⁸ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), Chap. IX.