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Optical Spectra and Paramagnetic Resonance of U^{4+} Ions in Alkaline Earth Fluoride Lattices*

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Paramagnetic resonance absorption measurements of uranium in various symmetries in CaF_2 and SrF_2 crystals are given. It is concluded that the centers seen in trigonal symmetry are U^{4+} ions. This conclusion is based on the observed direct correlation between the trigonal center resonance and one of two components which, generally speaking, together constitute the optical absorption spectra of these crystals. This spectral component is isolated and shown to agree with the published optical absorption spectra of U^{4+} compounds. Also, it is shown that the observed asymmetry of the trigonal center resonance and its zero $g_\perp$ value characterize the ground state $(f^2,{}^3H_4)$, in trigonal symmetry and cannot be properties of the state $(f^3,{}^4I_{9/2})$. A model is proposed for the U^{4+} center.

1. INTRODUCTION

IN a recent paper[1] Porto and Yariv reported measuring the paramagnetic resonance absorption of uranium centers in CaF_2 having trigonal symmetry about the ⟨111⟩ direction. These centers together with previously discovered ones having tetragonal symmetry about the ⟨100⟩ direction due to the presence of an extra F^- ion in the nearest interstitial site are the ones predominantly seen in paramagnetic resonance. The ratio of the numbers of the two types of centers varies considerably from sample to sample. Crystals with only traces of the trigonal centers present are used for continuous optical maser operation at 2.61 μ[2] and crystals in which the trigonal sites outnumber the tetragonal sites by 10:1 are reported to emit coherent radiation at 2.24 μ.[1] It had been assumed that the trigonal centers were U^{3+} ions charge compensated in some manner different from the tetragonal centers; however, no detailed models for the center were proposed.

In this paper evidence is presented that the above-mentioned trigonal centers which we have also observed by paramagnetic resonance in samples of CaF_2:U and, additionally, in samples of SrF_2:U are, in fact, not trivalent but tetravalent uranium ions. This fact is deduced in two separate ways. First, there is established a correlation between the intensity of the paramagnetic resonance absorption of the trigonal centers and the intensity of one of two components which, generally speaking, together constitute the optical absorption spectrum of these crystals. It is shown that this component of the optical absorption spectrum, when isolated, agrees with the published optical absorption spectra of tetravalent uranium compounds. Secondly, it is noted that the observed asymmetric paramagnetic resonance absorption line shapes as well as the observed zero $g_\perp$ value are both characteristic of the f^2 ground state configuration $^3H_4$ in a crystal field of trigonal symmetry. U^{4+} has a $5f^2$ configuration. U^{3+}, on the other hand, has a $5f^3$ configuration with a $^4I_{9/2}$ ground state and would split into 5 nondegenerate Kramers doublets in a trigonal field. This would result in symmetrical paramagnetic resonance line shapes and a finite $g_\perp$ value. Hence, from the nature of the paramagnetic resonance alone one can conclude that the trigonal symmetry centers are U^{4+} and not U^{3+} ions.

In Sec. 2 the optical absorption spectra of several CaF_2:U and SrF_2:U samples are shown. The two above mentioned components are clearly discernible in each case. Section 3 deals with the precise characteristics of the centers as measured by paramagnetic resonance.

2. OPTICAL ABSORPTION SPECTRA OF SrF_2:U AND CaF_2:U

The optical absorption spectra of uranium doped calcium fluoride and strontium fluoride crystals are, generally speaking, made up of two components, one arising from trivalent uranium centers and the other from tetravalent uranium centers. Figure 1 shows the optical absorption spectrum taken at 5°K on a sample of uranium-doped strontium fluoride in which almost 100% of the uranium ions are in the tetravalent state. This crystal was held at the melting point for only a short time, and as a result the uranium ions were not given time to be reduced. The crystal has the pale green color characteristic of tetravalent uranium ion absorption. Trivalent uranium ions always produce a deep red (CaF_2) or a deep orange-red (SrF_2) color because of intense absorption bands in the green.[3] Conway[4] has studied the absorption spectrum of U^{4+} ions in CaF_2 and his results, presented in tabular form, are roughly in agreement with the tetravalent uranium spectra shown in this paper. There is also general agreement between the positions of electronic levels which one can deduce from our spectra and those measured in the work of Satten, Young, and Gruen.[5] The last-mentioned refer-

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[1] S. P. S. Porto and A. Yariv, J. Appl. Phys. 33, 1620 (1962).

[2] G. D. Boyd, R. J. Collins, S. P. S. Porto, A. Yariv, and W. A. Hargreaves, Phys. Rev. Letters, 8, 269 (1962).

[3] L. N. Galkin and P. P. Feofilov, Doklady Akad. Nauk SSSR 114, 745 (1957) [translation Soviet Phys.—Doklady 2, 225 (1957)].

[4] J. G. Conway, J. Chem. Phys. 31, 1002 (1959).

[5] R. A. Satten, D. Young, and D. M. Gruen, J. Chem. Phys. 33, 1140 (1960).

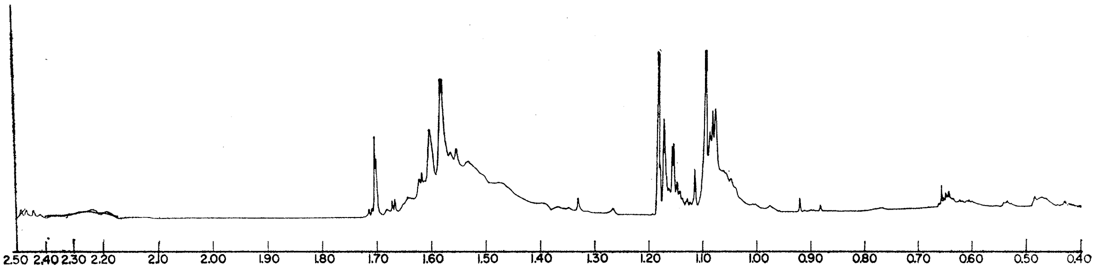

FIG. 1. Absorption spectrum at 5°K of SrF_2:100% U^{4+}, 0% U^{3+}. Wavelength is indicated in microns.

ence deals with the analysis of U^{4+} spectra in Cs_2UCl_6, $[N(CH_3)_4]_2UCl_6$, and $[N(C_2H_5)_4]_2UCl_6$. Strong bands at ≈ 1.05 and $1.55\,\mu$ are seen in both UCl_4 and UBr_4.[6] Finally, although they are weak in comparison with the infrared bands, the three visible region absorption bands which appear in Fig. 1 show a strong similarity to the absorption bands measured in the visible region for a number of other tetravalent uranium compounds.[7]

The sample whose absorption spectrum is shown in Fig. 1 is, as stated above, unique in that it gives no evidence of containing any trivalent uranium ions. For example, there is no indication of the sharp absorption at $1.88\,\mu$ that characterizes trivalent uranium ions in SrF_2. Thus, it may be assumed that the weak absorption bands in the region 2.2 to $2.5\,\mu$ in Fig. 1 are to be ascribed to transitions of U^{4+} ions. Conway[4] has also measured absorption in this region and ascribes it to transitions between the $^3H_4$ ground state and an excited state with term signature $^3F_2$. Conway states that there is no absorption at longer wavelengths; our measurements extend only to $2.5\,\mu$ and we were unable to check this point. However, if the lowest lying excited electronic levels of U^{4+} lie approximately 4000 to 5000 cm^{-1} above the ground state then the $2.24\,\mu$ maser action observed by Porto and Yariv in CaF_2 samples with trigonal to tetragonal ratios in excess of 10:1 might actually represent stimulated emission due to tetravalent uranium centers.

A SrF_2:U crystal containing mostly trivalent uranium has a spectrum as shown in Fig. 2(a). Figures 2(a) to (c)

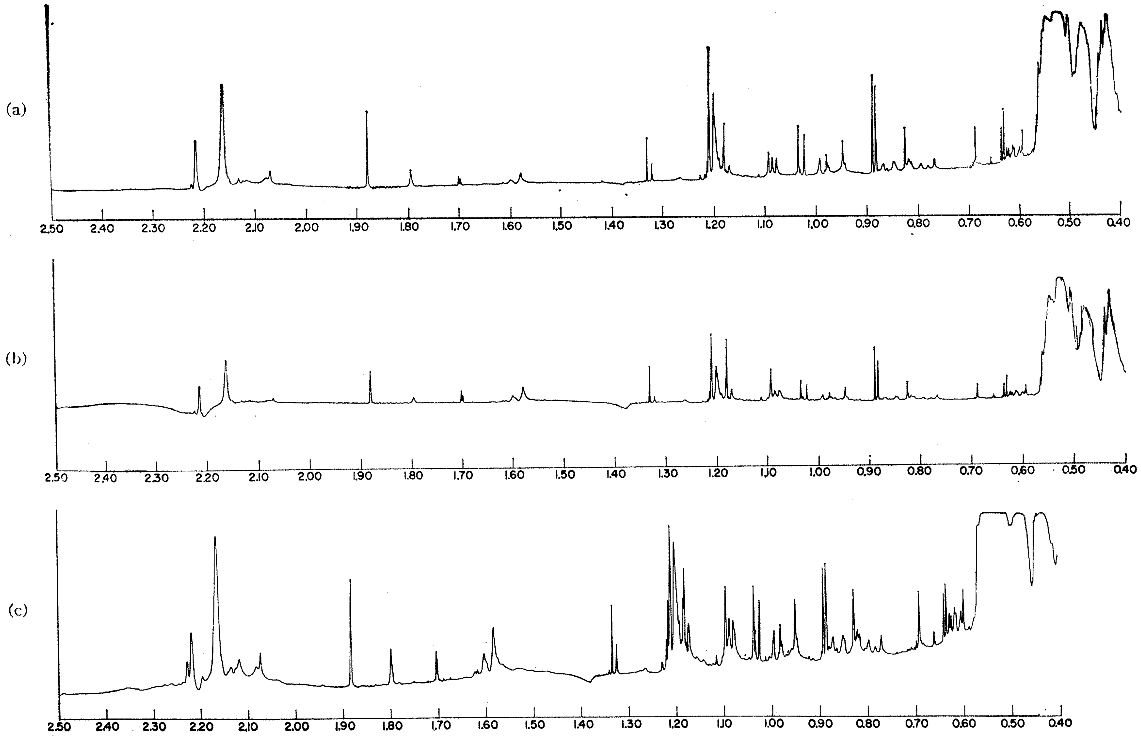

FIG. 2. Absorption spectra at 5°K of SrF_2:U samples with varying ratios of U^{4+} and U^{3+}. Wavelength is indicated in microns.

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[6] T. Dreisch and O. Kallscheuer, Z. physik. Chem. **B45**, 19 (1939).

[7] D. M. Gruen, J. Am. Chem. Soc. **76**, 3850 (1954).

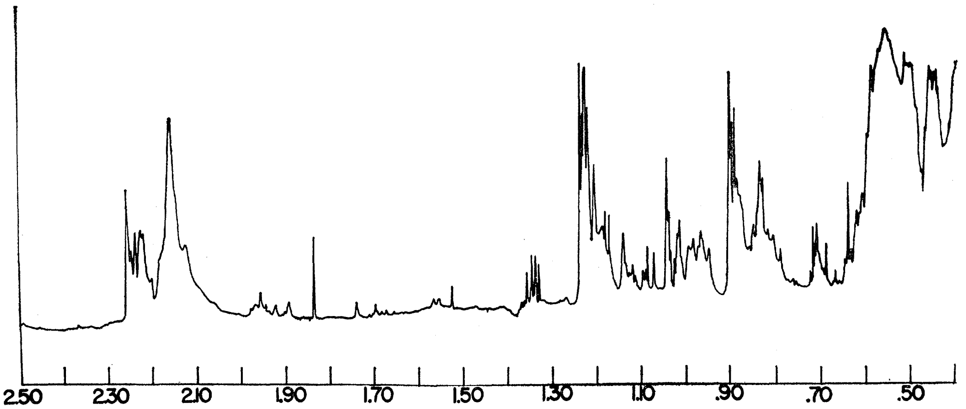

FIG. 3. Absorption spectrum at 5°K of CaF_2:U with relatively little U^{4+}. Wavelength is indicated in microns.

show absorption spectra of crystals with varying ratios of tetravalent and trivalent uranium.

Our paramagnetic resonance measurements corroborate Porto's and Yariv's reported finding of centers with trigonal symmetry having ⟨111⟩ oriented axes. The number of such centers in a given SrF_2:U sample is

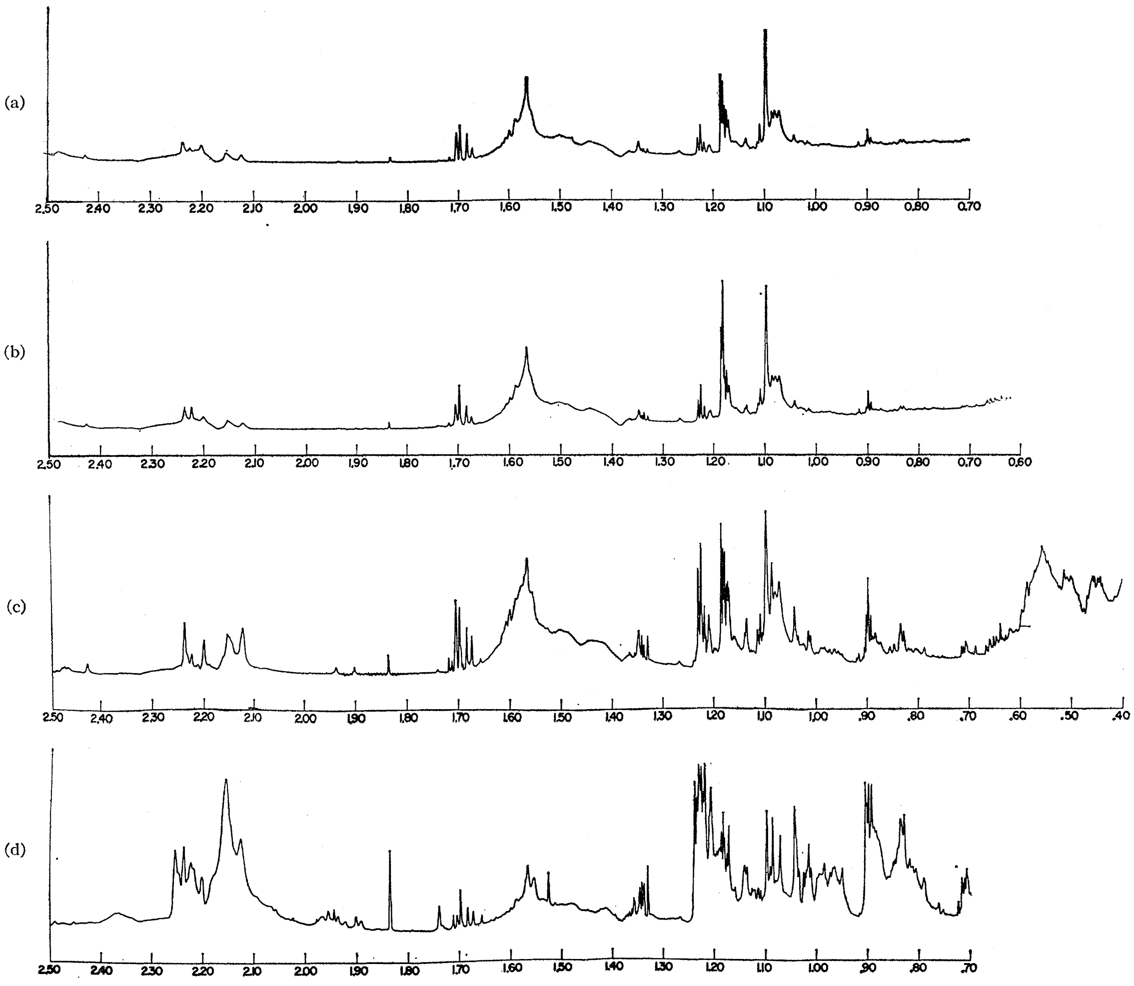

FIG. 4. Absorption spectra of CaF_2:U samples with varying ratios of U^{4+} and U^{3+}. Traces 4(a) ,4(b) are for the same sample at 5 and 77°K and show the relatively small line narrowing that occurs between 5 and 77°K. All other traces were taken at 5°K. The absorption coefficients are only approximately linear at wavelengths longer than 6000 Å. Wavelength is indicated in microns.

directly proportional to the strength of the 1.40 to 1.75 μ optical absorption. A similar situation holds for CaF_2:U. Thus, the symmetry of the tetravalent uranium centers in these crystals is known and a model for the center can be proposed. It is likely that a U^{4+} ion replaces a divalent calcium ion and two oxygen ions replace F^- ions at opposite corners of the surrounding cube of eight F^- ions. Charge compensation is accomplished in this manner. Moreover, this juxtaposition of ions is the same as in the stable compound UO_2 which has the fluorite structure and a lattice constant of 5.45 Å. CaF_2 has a lattice constant of 5.46 Å. The detailed characterstics of this U^{4+} center in both CaF_2 and SrF_2 as measured by paramagnetic resonance are set forth in the next section.

Figures 3 and 4(a) to 4(d) show optical absorption spectra for a number of CaF_2:U samples. The trivalent and tetravalent components can be easily distinguished. The crystal whose spectrum is shown in Fig. 3 contains relatively little tetravalent uranium. The sample whose spectrum is shown at 5 and 77°K in Figs. 4(a) and 4(b), respectively, contains a large percentage of tetravalent uranium. CaF_2:U crystals with the lowest thresholds for optical maser action have absorption spectra similar to that of Fig. 3. In these various figures only portions of the visible spectrum are shown. A figure which shows the entire optical spectrum of CaF_2:U containing only trivalent uranium is found in reference 2.

3. DETAILS OF PARAMAGNETIC RESONANCE ABSORPTION MEASUREMENTS

The CaF_2:U and SrF_2:U crystals that were measured show uranium to be present in various symmetries. In CaF_2:U trivalent uranium was observed in tetragonal symmetry and in cubic symmetry. In addition, the resonance of tetravalent uranium was observed in trigonal symmetry. This is the resonance that Porto and Yariv found and attributed to trivalent uranium. Some resonances of lower symmetry were also observed in CaF_2:U. In SrF_2:U the resonance of U^{3+} in tetragonal symmetry was observed as was that of U^{4+} in trigonal symmetry.

The tetragonal symmetry U^{3+} centers we observed in both CaF_2 and SrF_2 are the ones previously found by Bleaney *et al.*[8] Vincow and Low[9] have reported finding the resonance of U^{3+} in cubic symmetry. Their lines were weak and did not show the correct orientational dependence and hence their identification appears open to question. Results of our observations of U^{3+} in cubic symmetry are shown in Fig. 5. This gives the variation in the (110) plane of the two strongest transitions within the lowest lying quartet in cubic symmetry. The solid lines represent the theoretically predicted orientational dependence.[9,10] U^{3+} centers with cubic symmetry numbered about 10% of all observed centers in the average sample.

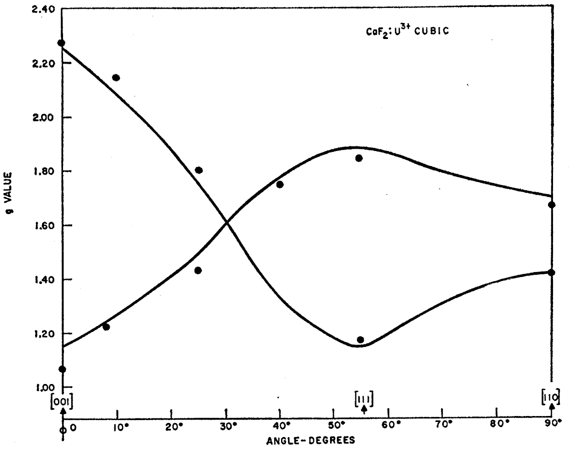

FIG. 5. Angular variation in the (110) plane of the two strongest transitions within the lowest lying quartet of U^{3+} in cubic symmetry in CaF_2.

The g values for the U^{4+} trigonal symmetry centers in CaF_2 were measured to be $g_{\parallel}=3.27\pm0.03$, $g_{\perp}=0\pm0.2$. These values agree with those measured by Porto and Yariv[1] who, however, attribute this resonance to U^{3+} ions, as stated above.

Figure 6 shows the resonances of the U^{4+} centers with trigonal symmetry in CaF_2. The derivative of the resonance absorption curve is recorded. The sharp peak is the resonance absorption of DPPH while those marked "*A*," "*B*," "*C*" are due to uranium. The magnetic field is oriented in the (110) plane in a position $3\frac{1}{2}°$ from the [001] axis. It is seen that the uranium resonance absorption curves are not symmetrical. Unlike the case of the DPPH resonance, the high-field sides of the uranium resonances are very much sharper than the low-field sides, leading to an emphasis of negative values in the derivative of the absorption curve. The resonances marked "*A*" and "*C*" are due to the U centers whose axes of trigonal symmetry are along the two [111] axes lying in the (110) plane of observation. There are two [111] type axes not in this plane and they give the resonance marked "*B*."

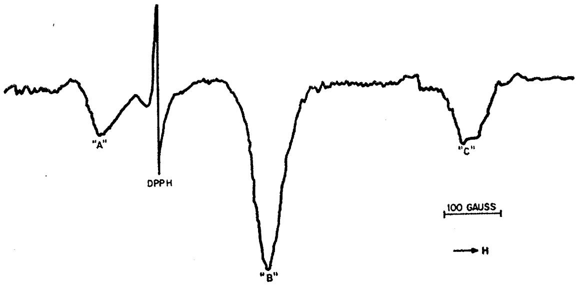

FIG. 6. Appearance of paramagnetic resonance traces of U^{4+} centers in CaF_2 when magnetic field is in the (110) plane $3\frac{1}{2}°$ from the [001] axis.

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[8] B. Bleaney, P. M. Llewellyn and D. A. Jones, Proc. Phys. Soc. (London) **B69** 858, (1956).

[9] G. Vincow and W. Low. Phys. Rev. **122**, 1390 (1961).

[10] B. Bleaney, Proc. Phys. Soc. (London) **73**, 939 (1959).

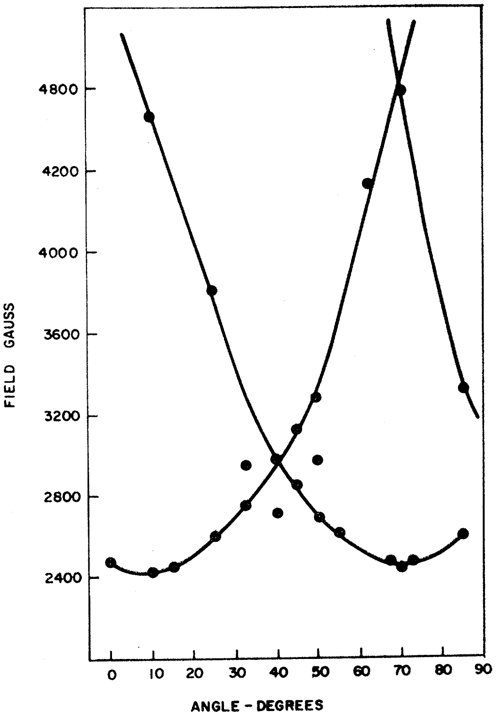

FIG. 7. Angular variation in a (111) plane of U^{4+} resonances in SrF_2.

U^{4+} centers in trigonal symmetry should yield resonances with the measured g values and with the observed line shapes, whereas U^{3+} centers in trigonal symmetry should not. The ground state of U^{4+} is $5f^2$, ${}^3H_4$. In a field of trigonal symmetry this state will split into three singlets and three doublets. The doublets are non-Kramers doublets and hence can be split by fields of lower symmetry. Such fields can arise from either small random strains in the crystal or else through lattice distortions arising from the Jahn-Teller effect. Such a split doublet will be characterized[11,12] by $g_\perp=0$ and, because of the random nature of the splitting, the resonance will have a line shape for the absorption curve that rises slowly on the low-field side and falls sharply on the high-field side.[11] This is precisely what is observed for the U resonances with trigonal symmetry and leads to the conclusion that the resonances are due to U^{4+} ions. Similar behavior was first observed for Pr^{3+} which has a $4f^2$ configuration.[13] By contrast, $U^{3+}(5f^3, {}^4I_{9/2})$ splits into five Kramers doublets in trigonal symmetry. Such doublets will yield lines of symmetrical shape and finite $g_\perp$.

The U^{4+} paramagnetic resonance spectrum with trigonal symmetry was also seen in crystals of SrF_2. U^{4+} was observed as the only paramagnetic center in the green colored SrF_2:U^{4+} crystal of Fig. 1. In Fig. 7, the variation of the resonance in a (111) plane is shown for this crystal. For centers of trigonal symmetry the value of g at the minimum is $\frac{1}{3}(8g_{\|}^2+g_\perp^2)^{\frac{1}{2}}$. At the same angle at which the minimum occurs a resonance should also be seen at $\frac{1}{3}(2g_{\|}^2+7g_\perp^2)^{\frac{1}{2}}$. From Fig. 7 it will be noticed that the resonances occurring at the angle at which there is a minimum, occur at fields in the ratio of 2:1 and hence have g values in the ratio of 1:2. This can occur only if $g_\perp=0$. The value of $g_{\|}$ is 2.87 ± 0.03. The resonances again have the asymmetrical shape and the g value is measured at the point on the high-field side of the line where the derivative goes to zero.

Further details of the uranium paramagnetic resonance spectra in CaF_2 and SrF_2 will be published elsewhere.[14]

Note added in proof. We have been informed by S. Porto and A. Yariv that since publishing the paper quoted in reference 1, they had independently reached the conclusion that the trigonal centers they observed were due to U^{4+} ions.

ACKNOWLEDGMENTS

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[11] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), pp. 135–6.

[12] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156, (1958).

[13] B. Bleaney and H. E. D. Scovil, Phil. Mag. 43, 999 (1952).

[14] R. S. Title, Proceedings of the First International Paramagnetic Resonance Conference, Jerusalem, July, 1962 (to be published).