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Luminescence of Hexavalent Uranium in CaF_2 and SrF_2 Powders

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A general investigation into the green luminescence of hexavalent uranium in calcium fluoride has been made in the temperature range 5 to 300°K. Two types of spectra have been found, due to different centers. Absorption spectra for these were also observed. The luminescent spectrum has been interpreted as a no-phonon line with vibrational structure on the sides. Assignment of the lines and bands observed has been made on the basis of lattice vibrations, internal local modes of the center, and combinations of these. It has been possible to fit the temperature dependence of the width and the position of the no-phonon line with a theoretical curve using the Debye temperature of the lattice determined from the specific heat. The spectrum of hexavalent uranium in strontium fluoride has many similarities, although it shows evidence of other electronic transitions in the luminescent spectrum.

I. INTRODUCTION

THE green luminescence of uranium in calcium fluoride has been known for some time.[1] Oxygen has been shown to be required in the preparation of a sample before any green luminescence will occur.[2,3] Kröger[4] has proposed a model of the luminescent center based on a hexavalent uranium atom replacing a calcium atom and four oxygen ions replacing four fluorine ions around the center to give the necessary charge compensation. At low temperatures the luminescent spectrum consists of lines superimposed on a band.[3] Apart from a decay-time measurement of the luminescence,[5] very little else appears to be known about the green luminescence of uranium in alkaline-earth fluorides, and so a preliminary investigation was made using calcium fluoride powders. The main results of this investigation are reported here, and this shows that there are marked concentration effects and also that the luminescent spectrum can be assigned as a no-phonon line[6] with accompanying vibrational structure. The temperature dependence of the no-phonon line is in agreement with some theoretical calculations.[6,7] Similarities in the spectral structure to that of the uranyl ion[8] and also of uranium in alkali fluorides[9] are pointed out.

II. EXPERIMENTAL

Powder samples of varying concentrations (percent uranium atoms to calcium atoms) were made by mixing together uranyl nitrate and calcium fluoride powders and firing them to about 1000°C. A crystal of strontium fluoride containing U^{4+} ions was also heated in air to give a luminescent sample, which had a very cloudy appearance, of approximately 0.01% concentration of uranium. Spectra of the samples were investigated on a Hilger large glass spectrograph for plates and photoelectric recordings of the spectra and of line shapes were taken on a 3.4-m Ebert spectrograph manufactured by the Jarrel Ash Company. The grating used in the 3.4-m spectrograph had a dispersion of 1.4 Å/mm in the sixth order in which the spectra were taken and this gave adequate resolution for the measurements made. Luminescence was excited by a mercury lamp with an

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[*] A Research Fund Fellowship was received from the New Zealand University Grants Committee.

[1] E. L. Nichols and M. K. Slattery, J. Opt. Soc. Am. 12, 449 (1962).

[2] I. P. Shapiro, Opt. i Spektroskopiya 7, 126 (1959) [English transl.: Opt. Spectry. (USSR) 7, 78 (1959)].

[3] P. Görlich, H. Karras, and R. Lehmann, Phys. Status Solidi 1, 525 (1961).

[4] F. A. Kröger, Physica 14, 488 (1948).

[5] N. A. Tolstoi and Liu Shun-Fu, Opt. i Spektroskopiya 13, 107 (1962) [English transl.: Opt. Spectry. (USSR) 13, 59 (1962)].

[6] D. E. McCumber, J. Math. Phys. 5, 221 (1964); 5, 508 (1964).

[7] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

[8] E. Rabinowitch and R. L. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds* (Pergamon Press, Inc., London, 1964).

[9] See A. A. Kaplyanskii, N. A. Moskvin, and P. P. Feofilov, Opt. i Spektroskopiya 16, 619 (1964) [English transl.: Opt. Spectry. (USSR) 16, 339 (1964)].

ultraviolet filter and absorption was studied photographically by reflection of light off the powders. A variable temperature Dewar, made by Andonian Associates, which could hold the sample at a fixed temperature to within 2°K, was used to study the temperature dependence.

III. THEORY

The theory for the no-phonon line transitions of impurity ions in solids[6,7] predicts the presence of a very sharp line (the no-phonon line), with accompanying vibrational side bands, in the spectrum. The interaction of the electronic system with the lattice phonons arises from the dynamic strains set up by the phonons. For a transition between two isolated electronic levels with a small interaction with the lattice phonons, the theory shows, using the approximations and assumptions of Ref. 6 and 7, that the shift $\Delta\omega$ in the position of the no-phonon line is given by

$$\Delta\omega(T)=\alpha\int_0^\infty \frac{d\omega}{2\pi}\rho(\omega)n(\omega), \tag{1}$$

and its width by

$$\Gamma(T)=\bar{\alpha}\int_0^\infty \frac{d\omega}{2\pi}[\rho(\omega)]^2 n(\omega)[1+n(\omega)], \tag{2}$$

where

$$n(\omega)=[\exp(\hbar\omega/kT)-1]^{-1}$$

is the thermal occupation number for the phonons and

$$\rho(\omega)=\sum_q |C_q|^2\delta(\omega-\omega_q)$$

is an effective density of states for the phonons. The phonon frequency and the coupling parameter for the qth mode are designated by ω_q and C_q, respectively. The effective density of states $\rho(\omega)$ represents the normal density of states weighted by the parameters $|C_q|^2$, and includes all vibrational modes of the lattice and impurity system.

For a Debye phonon spectrum

$$|C_q|^2=\hbar\omega/2\rho_m V\bar{v}^2$$

and

$$\rho(\omega)=\hbar\omega^3/2\pi\rho_m\bar{v}^5$$

for $0\leqslant\omega\leqslant\omega_D$, where the Debye temperature

$$\Theta_D=\hbar\omega_D/k;$$

ρ_m is the mass density of the crystal; V is the volume of the crystal, and $\bar{v}$ is the average sound velocity in the crystal. For this case Eqs. (1) and (2) become

$$\Delta\omega(T)=\alpha\frac{\hbar}{(2\pi)^2\rho_m\bar{v}^5}\left(\frac{k\Theta_D}{\hbar}\right)^4\left(\frac{T}{\Theta_D}\right)^4 \times\int_0^{\Theta_D/T}\frac{x^3dx}{e^x-1} \tag{3}$$

and

$$\Gamma(T)=\frac{\bar{\alpha}}{2\pi}\left(\frac{\hbar}{2\pi\rho_m\bar{v}^3}\right)^2\left(\frac{k\Theta_D}{\hbar}\right)^7\left(\frac{T}{\Theta_D}\right)^7 \times\int_0^{\Theta_D/T}\frac{x^6e^xdx}{(e^x-1)^2}. \tag{4}$$

If the phonon spectrum of the lattice can be approximated to a Debye spectrum then Eqs. (3) and (4) will describe the temperature dependence of the position and the width of the no-phonon line. The value of the Debye temperature, Θ_D, can be obtained from specific-heat data, and the agreement between the experimental data and Eqs. (3) and (4) will give some idea of the validity of the approximations used.

Equation (4) predicts a Lorentzian line shape which has zero width when $T=0$°K. However it is found experimentally that the no-phonon line has a finite width at zero temperature. This width most probably arises from static strain broadening[7] and it should be temperature-independent. The resulting no-phonon line shape is a Voigt profile,[10] and by using tables[11] it is possible to separate out the Lorentzian width. This has been done for the corrected points in Figs. 5 and 9 since only the Lorentzian width is predicted by Eq. (4).

On the side of the no-phonon line there are vibrational bands due to single- and multiphonon processes. At low temperatures only the single-phonon contribution is important and the band shape is of the form $\rho(\omega)/\omega^2$. (ω is the displacement frequency from the no-phonon line, and for the emission spectrum the band is on the low-energy side). The vibronic structure $\rho(\omega)/\omega^2$ may not show all the structure that is present in the phonon density of states for the lattice, since some phonons may be restricted from occurring by selection rules,[12] or the intensities may be small because of the $|C_q|^2$ term in $\rho(\omega)$.

If the lattice phonons are weakly coupled (i.e., $|C_q|^2$ small for them) then multiphonon processes due to them will generally be unimportant. However, if a local mode is strongly coupled to the electronic system it can give multiphonon effects with the lattice phonons. For a sharp local mode several phonons of it can appear in the vibronic spectrum and this will give a series of sharp lines which will also have accompanying vibronic structure, $\rho(\omega)/\omega^2$, similar to that for the no-phonon line. A local mode which is normally sharp, such as an internal mode of a complex center, may be broadened and will appear as such in the vibronic spectrum with its accompanying vibronic structure also broadened.

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[10] H. C. Van de Hulst and J. J. M. Reesinck, Astrophys. J. **106**, 121 (1961).

[11] D. W. Posener, Australian J. Phys. **12**, 184 (1959).

[12] R. Loudon, Proc. Phys. Soc. (London) **84**, 379 (1964).

IV. TYPE-I AND TYPE-II SPECTRA

Low-concentration powders show luminescent spectra similar to that in Ref. 2, and they are here designated as type I. An example of the luminescence spectrum is given in Figs. 1 and 2; it is characterized by a sharp no-phonon line at 19179 cm^{-1} (5212.7 Å) with vibrational structure on the side of it at low temperatures. Photographic records, at 77°K, show a weak anti-Stokes luminescence which is a mirror image of the Stokes luminescence.

The frequencies of the main peaks in the low-temperature luminescent spectrum can be represented by the equation

$$\nu = 19179 - 732k - n_i\nu_i \text{ cm}^{-1},$$

where $k=0$, 1, 2, 3, the intensity is very weak at $k=3$, ν_i is the frequency of a peak on the phonon spectrum $\rho(\omega)$ (see Sec. VI), the peaks are broadened out for $k \geqslant 1$ (see Fig. 2), and $n_i=0$ or 1, with higher values most probably occurring, but very weakly.

The vibration frequency of 732 cm^{-1} is ascribed to an internal local mode of the center. Covalent bonding of the oxygens with the uranium most probably occurs and the vibration is most likely to be the totally symmetric vibration of the complex formed by the bonds. For the uranyl ion[8] progressions with up to eight quanta of the totally symmetric vibration (about 860 cm^{-1}) are seen in some compounds. For hexavalent uranium in LiF and NaF[9], where uranium-oxygen bonds also most probably occur, a similar progression is seen, of 800 cm^{-1} and 708 cm^{-1}, respectively. A similar pattern is found for Ce^{+++} in CaF$_2$[13] where the local mode is about 480 cm^{-1} in both absorption and emission though only two quanta of it are reported (there may be others lost due to broadening). Similarities in the vibrational structure are discussed further in Sec. VI.

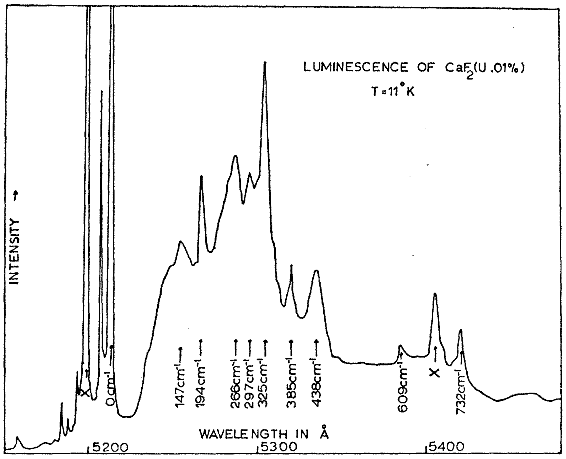

FIG. 1. Trace of the main vibrational structure in the type-I luminescent spectra of hexavalent uranium fluoride. The trace (as in the other figures) is not corrected for photomultiplier and instrument response. The main no-phonon line is designated as 0 cm^{-1} and the separation of the main peaks from this is given in terms of their energy (in cm^{-1}). Note the presence of weaker sharp lines around the no-phonon line. The lines marked X are at -51 and 682 cm^{-1}. They form an extra series of lines (see text)

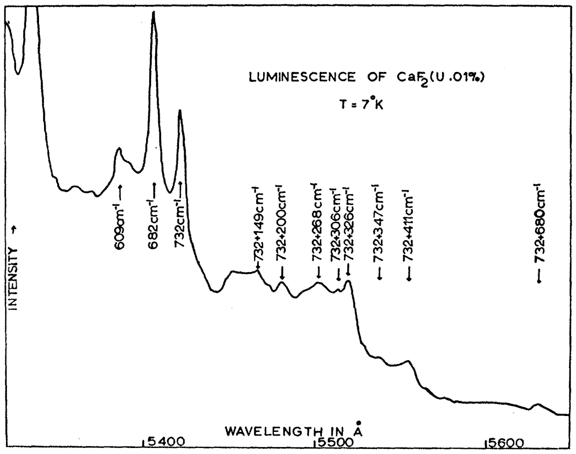

FIG. 2. An enlarged view of the first combination band in the type-I spectra.

Many powder samples show additional, usually weaker, no-phonon lines near the main one and their associated vibronic structure is too weak to be seen. However one line at 19230 cm^{-1} (5198.6 Å) often occurred with about the same intensity (even greater in some cases) as the 19179-cm^{-1} line. This line also is repeated at intervals of 732 cm^{-1}, though it does not seem to have any further phonon structure associated with it. These extra lines are most probably due to defects near the centers or interactions between centers close to each other. When the powders were reheated to about 1000°C and cooled slowly over a period of 24 h most of these extra lines disappeared from the spectrum.

At higher concentrations (i.e., 1%) the luminescent spectrum appears quite different and it is designated here as type II. This spectrum is characterized by two lines at 18936 cm^{-1} (5280.3 Å) and 18792 cm^{-1} (5320.5 Å), with a band on the low-energy side of them. A trace of the type-I spectrum is usually present in the form of the no-phonon line at 5212.7 Å (see Fig. 3). The spectra structure is repeated in a similar manner to that of the type I spectrum [see Eq. (5)], but here the local mode frequency is ~740 cm^{-1}. (It is not well defined owing to considerable broadening.) This frequency is also ascribed to an internal mode of the complex forming the center.

As the concentration of uranium is increased there is a gradual change from the type-I to the type-II luminescent spectrum with the over-all intensity of the luminescence appearing to remain fairly constant. The presence of type II is first detected at a concentration of about

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[13] A. A. Kaplyanskii, V. N. Medvedev, and P. P. Feofilov, Opt. i Spektroskopiya 14, 664 (1963) [English transl.: Opt. Spectry. (USSR) 14, 351 (1963)]. For a spectral trace see C. W. Struck and F. Herzfeld [J. Chem. Phys. 44, 464 (1966)] who, however, give a different interpretation to the vibrational structure.

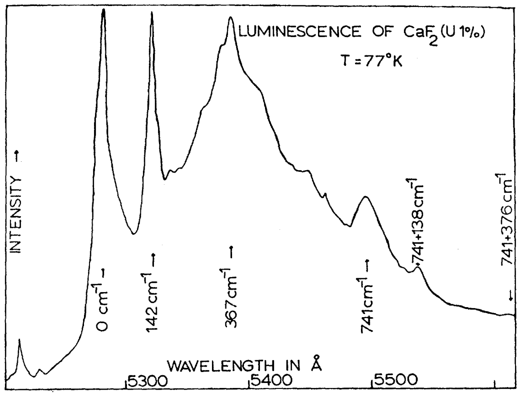

FIG. 3. Type-II luminescent spectra of hexavalent uranium in calcium fluoride. The presence of type I is shown by the line at 5212.7 Å.

0.1%. At about 10% concentration only a broad band is left. The interpretation of these concentration changes is as follows: As the concentration of uranium increases the formation of a second type of center becomes favorable. An absorption band due to the type-II center overlaps the luminescent spectrum of type I, so that light emitted by type I can be absorbed (especially in a powder where many reflections can occur) and appear as light emitted by type-II centers. Thus the spectrum can appear to consist largely of type II even though there are a considerable number of type-I centers present as can be seen from the absorption spectrum.

It is possible to obtain an absorption spectrum photographically from the powders by diffuse reflection methods. The absorption is very weak except in high concentration samples when it is a broad band, and no detailed structure could be obtained from it. For type-I spectra the 19179-cm^{-1} line also appears in absorption with a weak vibrational structure on the high-energy side. Some of the frequency intervals in this appear to be similar to those found in the luminescent spectrum. As the absorption for type-I centers is very weak, higher concentration samples are required to detect it, but these have the type-II absorption spectrum overlapping it, thereby increasing the difficulty in assigning the spectrum. The type-II spectrum shows the 18934-cm^{-1} line in absorption with a vibrational structure which overlaps that of the type-I spectrum.

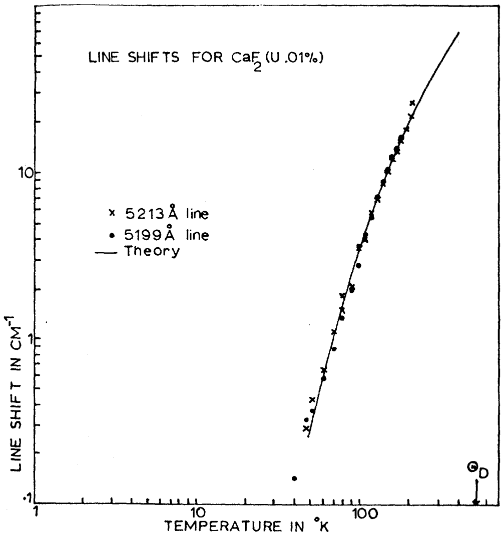

FIG. 4. Line shifts for no-phonon lines in type-I spectra. The agreement between theory and experiment is well within the possible experimental errors.

Other absorption spectra which are ascribed to the uranium center are a sharp line at 9148 Å and a weak broad band centered at 3402 Å. This band is the one used for the excitation of the luminescence, which could also be excited in the absorption band near the 19179-cm^{-1} line.

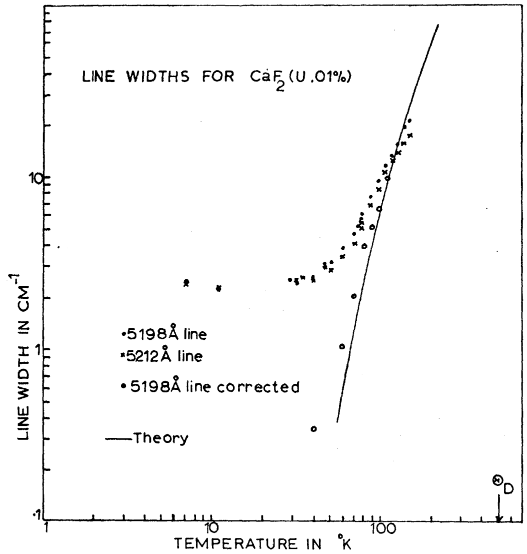

FIG. 5. Linewidths of the no-phonon lines for type-I spectra. The corrected values were made on the basis of a residual linewidth of 2.4 cm^{-1}. The agreement is within the possible experimental error which is greater here, than for the line shifts, because of the corrections needed.

V. NO-PHONON LINES

To test whether the sharp lines observed (at 5212.7 and 5198.6 Å) fit the no-phonon line theory,[6,7] their widths and shifts were measured photoelectrically as a function of temperature. The widths used are those at half intensity after subtraction of any possible background due to neighboring bands or lines. Figures 4 and 5 give the results for one of the low-concentration samples, with a comparison with the theory of Eqs. (3) and (4). The Debye temperature Θ_D is taken from specific-heat data[14] as 510°K (at 0°K), and α and $\bar{\alpha}$ taken to

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[14] D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).

fit values at about 100°K. As can be seen this gives quite a good fit to the data. A slightly better fit could be made by making Θ_D smaller. For H^- ions in CaF_2 a value of 425°K is used to fit the line shifts.[15] In the case of ruby[7], a Θ_D considerably less than the specific-heat value is required.

As can be also seen from Figs. 4 and 5 the two no-phonon lines have identical linewidths at all temperatures, within experimental error, and this is also true for other weaker no-phonon lines often observed. The line shapes at low temperatures, however, are not always exact Voigt profiles. This suggests some other broadening process, possibly due to nonrandom strains, is present in the powders. The residual linewidth is about 2.4 cm^{-1} compared to about 0.1 cm^{-1} found in ruby crystals.[7]

VI. PHONON BANDS

Most of the values of ν_i in the vibrational structure [see Eq. (5)] can be assigned to lattice phonons of calcium fluoride, i.e., $\rho(\omega)$ reflects the phonon density of states for the host lattice. Table I lists the main peaks (see Figs. 1 and 2) with a possible assignment of the phonons based on the lattice data in Refs. 16–18 (notaton is that of Ref. 18). These assignments must be tentative until more data on the lattice dynamics of calcium fluoride are available.

TABLE I. Lattice phonons of calcium fluoride in vibronic spectra.

Uranium (cm^{-1})	Assignment (cm^{-1})	Ce^{+++} (cm^{-1})
147	$TA(X)=150$	167
194	$TO^a(X)=217$	200
...		231
266	$TO^a(L)=270$	...
297	$TO^b(L)=300$	302
325	$TO^b(X)=327$	330
385		387
435		432

A comparison with the main peaks in the absorption spectrum of Ce^{3+} in calcium fluoride,[13] at 31965 cm^{-1}, is also given in Table I. There is a close agreement between the two systems with only one major difference in that a peak at 266 cm^{-1}, in the case of uranium, does not occur for Ce^{3+} but rather a peak at 231 cm^{-1} occurs. Comparison with the spectra of the divalent rare earths, Eu^{2+}, Tm^{2+}, and Sm^{2+} ions in calcium fluoride[19] shows that the peak at about 230 cm^{-1} is fairly common and probably belongs to the lattice. Two other peaks at about 195 cm^{-1} and 385 cm^{-1} are also common to these rare-earth spectra.

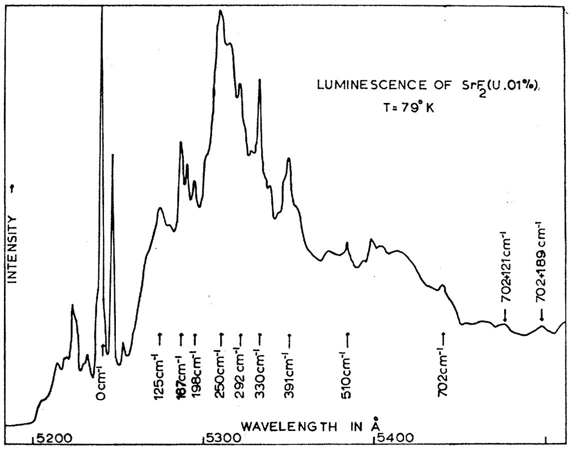

FIG. 6. Luminescence spectra of hexavalent uranium in a crystalline sample of strontium fluoride at 79°K. Lines are assigned on a similar basis to that for Fig. 1.

The vibrational frequencies at 609 and 732 cm^{-1} are too high for the lattice phonon modes and most likely belong to internal modes of the center. The value at 682 cm^{-1} is just the combination of 732 cm^{-1} with the second no-phonon line (at -51 cm^{-1} in Fig. 1) and is absent in samples in which the second no-phonon line is not present. Other internal modes may be present and these could easily be in resonance with lattice modes to give an enhancing of some phonon peaks.

VII. $SrF_2(U)$ LUMINESCENCE

The luminescence of a crystalline sample of strontium fluoride containing some hexavalent uranium (approximately 0.01%) was also studied for comparison. This luminescent spectrum (see Figs. 6 and 7) has many similarities to that for calcium fluoride and it also has some striking differences.

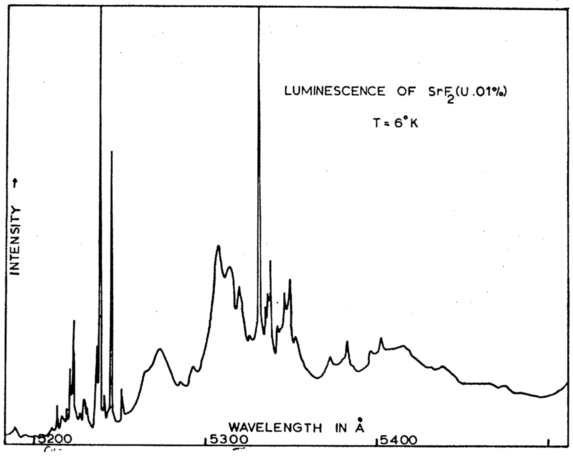

FIG. 7. Luminescence of SrF_2(U) at 6°K. This shows marked differences to that for 79°K (see Fig. 6) though most of the peaks are in the same positions.

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[15] S. S. Mitra and R. S. Singh, Phys Rev. Letters **16**, 694 (1966).

[16] D. Criber, B. Farnoux, and B. Jacrot, *Inelastic Scattering of Neutrons in Solids* (International Atomic Energy Agency, Vienna, 1963), Vol. II, p. 225.

[17] S. Ganesan and R. Srinivasan, Can. J. Phys. **40**, 74 (1962).

[18] S. Ganesan and E. Burstein, J. Phys **26**, 645 (1965).

[19] M. V. Hobden, Phys. Letters **15**, 10 (1965).

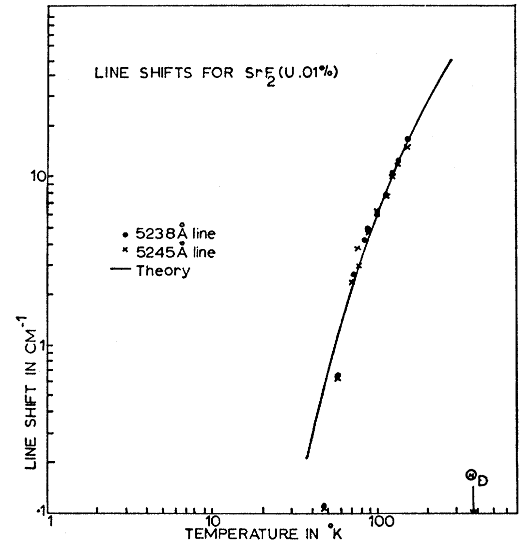

FIG. 8. Lines shifts for the no-phonon lines in the luminescent spectra of $SrF_2(U)$. Agreement with the theory is within experimental error.

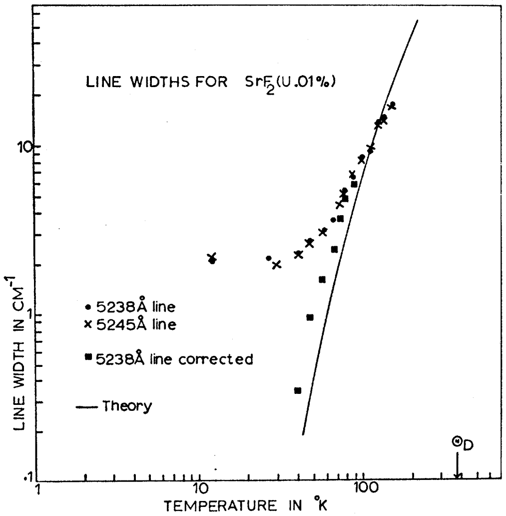

FIG. 9. Linewidths of the no-phonon lines in the luminescent spectra of $SrF_2(U)$. The corrected values were made on the basis of a residual linewidth of 2.1 cm^{-1}. Errors are similar to that for Fig. 5.

It exhibits no-phonon lines with a vibrational structure in a similar manner to that of $CaF_2(U)$, the main line being at 5238.3Å (19085 cm^{-1}). The temperature dependence of the no-phonon lines can be fitted by Eqs. 3 and 4 (see Figs. 8 and 9). The value of Θ_D is taken from a Debye temperature calculation from elastic-constant data[20] to be 380°K (at 0°K), and this value is expected to be similar to that from specific-heat data.

Assuming that the assignments given the lattice phonons for calcium fluoride to be correct then the corresponding values for strontium fluoride are $TA(X)=125$ cm^{-1}, $TO^a(X)=198$ cm^{-1}, $TO^a(L)=250$ cm^{-1}, $TO^b(L)=268$ cm^{-1}, $TO^b(X)=292$ cm^{-1}, and 702 cm^{-1} is the internal local mode which combines with these.

The main difference between the luminescent spectra of $CaF_2(U)$ and $SrF_2(U)$ is in the temperature dependence of the vibrational structure. $CaF_2(U)$ luminescence shows little change, apart from the narrowing of some lines, on going from 79 to 6°K. However, as seen in Figs. 8 and 9, there is a marked change in the $SrF_2(U)$ luminescence. The main feature of the change is the "freezing" out of a group of lines near 167 cm^{-1} (and their combinations with 702 cm^{-1}), while another group near 330 cm^{-1} (and their combinations with 702 cm^{-1}) increases markedly in intensity. The line at 330 cm^{-1} (or 5330.7Å) is as sharp as the no-phonon line. Its shift with temperature is opposite to that of the other no-phonon lines, and this suggests that it is a second electronic transition or possibly a temperature-dependent local mode.

The presence of this second electronic transition complicates the spectrum and makes further assignments difficult at present. Further complications also arise since the weaker no-phonon line (at 5245Å) has a vibrational structure which shows up as weak peaks near the main ones.

No absorption spectrum could be found and it is most probably too weak to pick up at this concentration, as is the one for $CaF_2(U)$.

VIII. CONCLUSION

The spectra of hexavalent uranium in alkaline-earth fluorides still needs further work for its clarification. Further work on single crystals using stress and polarization experiments is needed, especially to help establish a possible electronic system. A comparison with the luminescence of some rare-earth ions suggests that transition is of the form $f^{n-1}\,d\rightarrow f^n$. Hexavalent uranium has no f electrons but the oxygen present for charge compensation may donate electrons to it, giving perhaps a f^1 or f^2 configuration.

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[20] D. Gerlich, Phys. Rev. **136**, A1366 (1964).