lattice site

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|i\rangle=\langle\Gamma_1{}^+|\delta(\mathbf{r}-\mathbf{R}_5)|\Gamma_{4z}{}^-\rangle$$

$$=\left\langle\frac{1}{\sqrt{6}}(\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6)\right.$$

$$\left.\times|\delta(\mathbf{r}-\mathbf{R}_5)|\frac{1}{\sqrt{2}}(\phi_5-\phi_6)\right\rangle$$

$$=(2\sqrt{3})^{-1}|\phi_5|^2 \qquad (51)$$

and

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|0\rangle=\langle\Gamma_1{}^+|\delta(\mathbf{r}-\mathbf{R}_5)|\Gamma_1{}^+\rangle$$
$$=\tfrac{1}{6}|\phi_5|^2. \qquad (52)$$

By using Eqs. (50)–(52) in Eq. (43) we get

$$|\Delta a|=(\partial a/\partial E)E=2ea\Delta^{-1}E\{[(2\sqrt{3})^{-1}$$
$$\times(2R_0-4\gamma)^{1/2}(1-\gamma)^{1/2}(32R_0)\xi^{3/2}\xi'^{5/2}(\xi+\xi')^{-5}]$$
$$\times[(2\sqrt{3})^{-1}|\phi_5|^2][\tfrac{1}{6}|\phi_5|^2]^{-1}\}$$

or

$$(\partial a/\partial E)=ea\Delta^{-1}[2R_0-4\gamma^{1/2}(1-\gamma)^{1/2}$$
$$\times(32R_0)\xi^{3/2}\xi'^{5/2}(\xi+\xi')^{-5}] \qquad (53)$$

or

$$\partial a/\partial E\simeq 2eaR_0\Delta^{-1}\times 10^{-2}\ \mathrm{Hz/V\ cm^{-1}}. \qquad (54)$$

Here R_0 is expressed in Å and a, the isotropic hyperfine interaction constant, is in MHz. To arrive at Eq. (54) we have neglected the second term in Eq. (53) which introduces an error of about 2 to 4%.

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Sharp-Line Luminescence of Re^{4+} in Cubic Single Crystals of Cs_2ZrCl_6 and Cs_2HfCl_6†

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Sharp-line luminescence has been observed for Re^{4+} ($5d^3$) in single crystals of Cs_2ZrCl_6 and Cs_2HfCl_6 at low temperature. Well-resolved vibronic structure is seen, forming nearly perfect mirror symmetry between emission and absorption about a zero-phonon line at 13 879 cm^{-1}. Using the assignments of Dorain and Wheeler, these are identified as being due to transitions within the $t_{2g}{}^3$ configuration from the $\Gamma_7(^2T_{2g})$ level to the ground state $\Gamma_8(^4A_{2g})$. Vibrational energies of the odd modes of the $ReCl_6{}^{2-}$ complex are found to be the same for both the ground and excited states. The flourescence lifetime of 100 μsec at 2 K suggests the presence of other modes of decay than the observed luminescence. The luminescence can be excited either by transitions into the electric dipole allowed levels arising from t_2e configuration or to the $\Gamma_8(^2T_{2g})$, ($t_2{}^3$) levels.

SHARP-LINE optical spectra of impurities in solids are known to exist primarily for the rare-earth ions and a few special cases of the $3d$ transition series.[1] The states between which the transitions take place are usually of the same configuration within an electronic shell that is shielded from interactions with the crystal electric field and with neighboring ions. These transitions which are usually forbidden for free atoms become allowed in low-symmetry electric fields or in higher-symmetry fields with the cooperation of the odd modes of vibration associated with the ion's ligands or the crystal lattice. In addition to the examples of the $3d$ transition metals, it has been shown, by Dorain and his co-workers,[2,3] that sharp-line absorption spectra are also observed when the $5d$ ions, Re^{4+} and Os^{4+}, are present in dilute concentration as impurities in suitable crystal hosts. Dorain and Wheeler[2] show that the absorption spectra of Re^{4+} in K_2PtCl_6 and Cs_2ZrCl_6 could be explained on the basis of crystal-field theory applied to the $ReCl_6{}^{2-}$ complex in a slightly distorted cubic lattice. Detailed information about the crystal-field, Racah, and spin-orbit parameters were obtained along with the magnetic properties of the low-lying states, the odd-mode vibrational energies associated with the electronic levels, and the nature of the electronic transition, i.e., electric or magnetic dipole. This paper reports the observation of narrow-line *luminescence* of Re^{4+} present as an impurity in the cubic crystals Cs_2HfCl_6 and Cs_2ZrCl_6. This system is particularly interesting since Re^{4+} is isoelectronic with Cr^{3+}, whose luminescence spectra have been the subject of many investigations.

At low temperature the luminescence spectrum reported here consists of four lines between 7000 and 7400 Å. The transitions are identified using the assignments of Dorain and Wheeler as originating from the $\Gamma_7(^2T_{2g})$ level of the $t_{2g}{}^3$ configuration of Re^{4+} and

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[1] See, for example, Gerhard H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley-Interscience, Inc., New York, 1968); D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 9.

[2] P. B. Dorain and R. G. Wheeler, J. Chem. Phys. **45**, 1172 (1966).

[3] P. B. Dorain, H. H. Patterson, and P. C. Jordan, J. Chem. Phys. **49**, 3845 (1968).

terminating on the ground state $\Gamma_8({}^4A_{2g})$, $t_{2g}{}^3$. Coupling of the electronic state with a number of the odd vibrational modes of the $ReCl_6{}^{2-}$ complex produces the observed structure.

Crystals of Cs_2ZrCl_6 and Cs_2HfCl_6 containing the Re^{4+} were grown by the method described by Dorain *et al.*[2] and by Axe.[4] The boules were not very uniform in structure but contained small, clear, green regions which could be cleaved out and were sufficient for luminescence and absorption measurements. The Re concentration was measured by emission spectroscopy to be 1000–5000 ppm. The luminescence was excited by a 100-W short-arc mercury lamp which was first dispersed by a quartz-prism monochromator. The samples were held in a standard optical Dewar and the front-surface luminescence spectra were observed with a $\frac{3}{4}$-m grating spectrometer equipped with a cooled RCA 7102 photomultiplier utilizing phase-sensitive detection. Absorption spectra were taken with the same apparatus, replacing the mercury lamp and monochromator with a 45-W quartz iodine lamp. Luminescence decay time was measured either by pulsing the excitation lamp or by using a small, xenon flash lamp. In the former case, sufficiently high repetition rates and stability were achieved to make use of signal-averaging techniques although these were only used to check the results obtained by direct measurement.

The observed luminescence spectrum of Re^{4+} is best understood with reference to the energy-level diagram given by Dorain and Wheeler.[2] For convenience, this is reproduced in Fig. 1 along with a more detailed representation of the levels involved in the luminescence transition. The latter are the ground state which is $\Gamma_8({}^4A_{2g})$ and the excited level $\Gamma_7({}^2T_{2g})$ and their associated vibrational structure. The low-temperature absorption and the luminescence of Re^{4+}-doped Cs_2ZrCl_6 at several temperatures are shown for comparison in Fig. 2. The spectra of Cs_2HfCl_6 (not shown) is essentially identical except it is shifted approximately 15 cm^{-1} to lower energy.

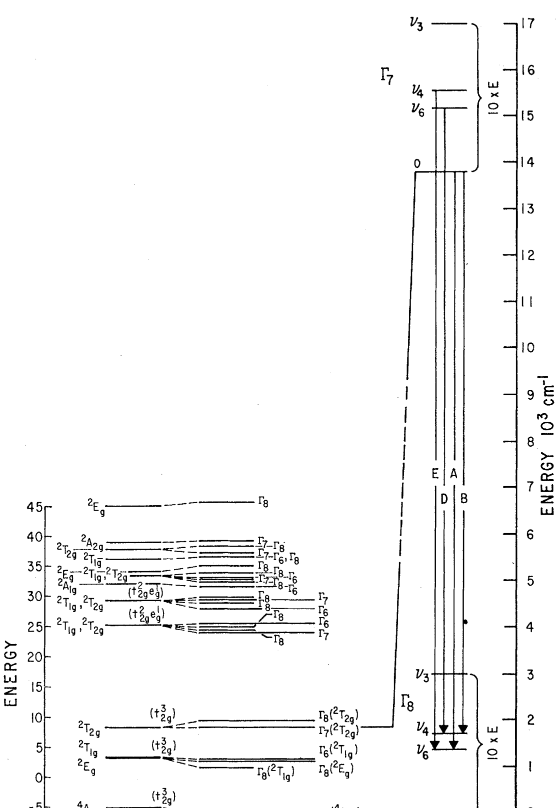

FIG. 1. Energy-level diagram for $Re^{4+}(d^3)$ in a cubic octahedral field (after Dorain and Wheeler, Ref. 2). The right-hand side of the figure shows details of the vibrational structure for those levels involved in the observed luminescence. The lettered transitions correspond to those given in Table I. For clarity only four of the observed transitions are shown.

TABLE I. Observed positions and identification of transitions of Re^{4+} in Cs_2ZnCl_6. The primed letters indicate absorption. All others are luminescence.

Figure	Peak	Observed energy (cm^{-1})	Description
1(a)	*O′*	13 879	${}^4A_{2g}(0) \rightarrow {}^2T_{2g}(0)$
1(a)	*A′*	14 014	${}^4A_{2g}(0) \rightarrow {}^2T_{2g}(\nu_6)$
1(a)	*B′*	14 052	${}^4A_{2g}(0) \rightarrow {}^2T_{2g}(\nu_4)$
1(a)	*C′*	14 186	${}^4A_{2g}(0) \rightarrow {}^2T_{2g}(\nu_3)$
1(b)	*O*	13 879	${}^2T_{2g}(0) \rightarrow {}^4A_{2g}(0)$
1(b)	*A*	13 742	${}^2T_{2g}(0) \rightarrow {}^4A_{2g}(\nu_6)$
1(b)	*B*	13 706	${}^2T_{2g}(0) \rightarrow {}^4A_{2g}(\nu_4)$
1(b)	*C*	13 567	${}^2T_{2g}(0) \rightarrow {}^4A_{2g}(\nu_3)$
1(c)	*D*	13 845	${}^2T_{2g}(\nu_6) \rightarrow {}^4A_{2g}(\nu_4)$
1(c)	*E*	13 916	${}^2T_{2g}(\nu_4) \rightarrow {}^4A_{2g}(\nu_6)$
1(d)	*F*	14 019	${}^2T_{2g}(\nu_6) \rightarrow {}^4A_{2g}(0)$
1(d)	*G*	14 054	${}^2T_{2g}(\nu_4) \rightarrow {}^4A_{2g}(0)$
1(d)	*H*	14 187	${}^2T_{2g}(\nu_3) \rightarrow {}^4A_{2g}(0)$

The most striking feature of the data is that at low temperature the luminescence and absorption spectra form highly symmetrical mirror images of each other. This symmetry clearly establishes the identity of the transitions as due to a single zero-phonon transition and associated vibronic structure, and further substantiates the energy-level description previously given by Dorain and Wheeler.[2] Using their notation, the energy of each of the transitions and their description is given in Table I. The left side of the description column is the initial state and its phonon symmetry and the right-hand side describes the final state. The assignments which we give for the observed spectra are slightly different than those of Dorain and Wheeler.[2] They observed only a single absorption line in the vicinity of 14 055 cm^{-1} in Cs_2ZrCl_6 and assigned it to the ν_3 mode. This is due to the low concentration they employed in

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[4] J. D. Axe, H. J. Stapleton, and C. D. Jeffries, Phys. Rev. **121**, 1630 (1961).

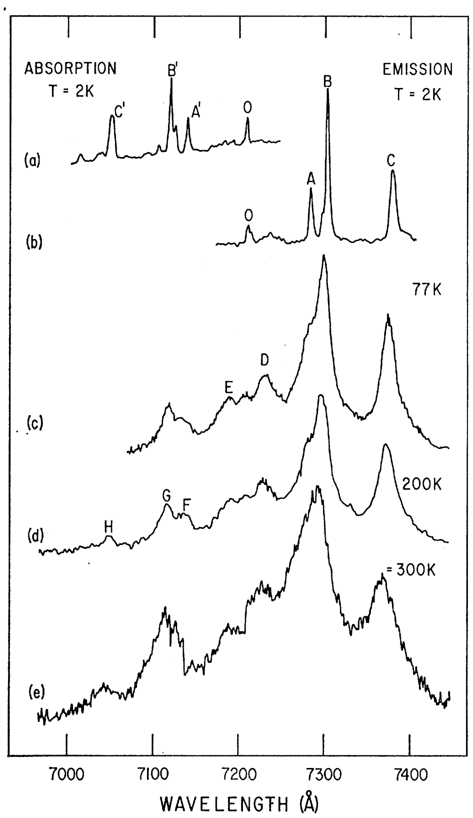

FIG. 2. Observed absorption spectrum at 2 K and luminescence spectra from 2–300 K for Cs$_2$ZrCl$_6$:Re. The lettered transitions correspond to those in Table I.

order to see resolved absorption to the higher energy levels. Both of our luminescence and absorption results suggest that this transition which we observe at 14 052 cm^{-1} is actually due to the ν_4 vibration. The change in host environment from K$_2$PtCl$_6$ to Cs$_2$ZrCl$_6$ then results in a shift of $\sim+50$ cm^{-1} rather than -100 cm^{-1} as previously reported in Ref. 2. In addition to the transitions identified in Table I, several weak lines are observed between the 0–0 and the $0-\nu_6$ transitions in both emission and absorption at 2 K. These have been attributed to lattice modes of Cs$_2$ZrCl$_6$[3] other than those identified in the main part of the spectrum, but are not considered further here.

As the temperature of the sample is increased from 2 K, additional luminescence lines are observed which arise from the thermally excited vibrational states of $\Gamma_7(^2T_{2g})$. These are shown in Figs. 2(c)–2(e) and listed in Table I as *D* through *H*. Lines *F*, *G*, and *H* correspond to the phonon-assisted transitions that are seen in low-temperature absorption. Within the accuracy of the measurement, the absolute positions of both sets of lines are in good agreement. In addition to transitions for which the complex ends up in its ground vibrational level two lines are readily identified as arising from a change from a ν_3 to ν_4 vibrational state and conversely. These are shown as lines *D* and *E* in Table I and Fig. 1. As the temperature is increased all the lines continue to broaden and the thermally excited components increase in intensity according to their respective Boltzmann population.

The energy differences of the three strong lower-energy emission lines from the one marked *O* are the frequencies of the vibrational modes $\nu_6(t_{2u})$, $\nu_4(t_{1u})$, and $\nu_3(t_{1u})$, respectively. These are the odd internal vibrations of the ReCl$_6^{2-}$ complex and have been discussed in detail by Pollack.[5] As such, they are not expected to show much variation among the different host lattices investigated so long as the mass of the ligands does not change greatly and the symmetry of the complex remains unchanged. A comparison of the vibrational energies in the ground $^4A_{2g}$ level and the excited $\Gamma_7(^2T_{2g})$ level as determined by emission and absorption, respectively, show that they are essentially identical. This is a consequence of the transition being between states contained within the t_{2g}^3 manifold so that the radial wavefunction remains unchanged. The equilibrium nuclear separation is then the same for the ground and excited states and the vibrational energy corresponding to a particular symmetry remains unchanged.

The fluorescent lifetime was determined to be 100 μsec at 2 K and decreased to 60 μsec at 77 K and remained constant to 300 K. On the basis of the absorption measurements, the oscillator strength for the transition involving the ν_3 vibration, for example, is estimated to be $f=\sim3\times10^{-6}$. This leads to a radiative lifetime of approximately 1.3×10^{-3} sec. In the absence of a more accurate value for the oscillator strength it is not possible to determine if the measured lifetime consititutes a significant departure from this value. Attempts were made to observe luminescence transitions from other levels. This, however, was unsuccessful using the *S*1 photomultiplier system described above.

Several infrared emission lines were observed with another luminescence apparatus which utilized a prism spectrograph and an InAs detector. They were at approximate energies of 7463, 6024, and 4630 cm^{-1}, the strongest transition being at 6024 cm^{-1}. Because of the low resolution of this instrument, no detailed vibronic structure was resolved. Without this information it is difficult to make definite assignments for these lines. We can, however, estimate the position of the $\Gamma_8(^2T_{1g},\nu_3)$ level from Dorain as being at about 7875 cm^{-1}. This predicts that the transition $\Gamma_7(^2T_{2g})\rightarrow\Gamma_8(^2T_{1g})+\nu_3$ should occur at 6004 cm^{-1} in reasonable agreement with the observed luminescence at 6024 cm^{-1}.

Although no detailed excitation spectra were taken, two distinct excitation regions could be distinguished which can be correlated with the absorption spectrum in Cs$_2$ZrCl$_6$. One is a high-energy band beginning at about 3800 Å and extending to higher energies. This corresponds to the onset of electric dipole allowed absorption into the energy levels of the $t_{2g}^2e_g^1$ configuration.

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[5] S. A. Pollack, J. Chem. Phys. **38**, 98 (1963).

Luminescence could also be excited with reasonable efficiency by exciting in a broad band centered near 6500 Å. This undoubtedly corresponds to absorption into the $\Gamma_8(^2T_{2g})$ levels which could be seen in the absorption spectra reported by Dorain and also in our own samples. The measured lifetime was independent of the excitation wavelength. It is interesting to speculate on the nature of the excitation that leads to the luminescence particularly when the crystal is excited with ultraviolet light. In this case the excited state is at least 15 000 cm^{-1} higher in energy than the nearest state that is within the t_2^3 configuration. This seems to be a rather large energy difference to be accounted for by a multiphonon relaxation unless there is considerable lattice relaxation within the excited state to which the transition initially occurs. Dorain and Wheeler give a value of 7% for the change in Re—Cl bond length for transitions to states of $t_{2g}{}^2e_g$ configuration. We can use this value to obtain a crude estimate of the decrease in energy of the lowest level of the $t_{2g}{}^2e_g$ configuration due to the change in crystal-field strength with dilation. A 7% change in bond length (assumed to be an expansion) leads to a decrease in crystal field of nearly 30%. Since in the region of large crystal fields the energy of the $^2T_{2g}$ levels is directly proportional to the strength of the field, this leads to a reduction in energy of this level likewise by about 30%. This is a decrease of some 10 000 cm^{-1} to an energy only 5000 cm^{-1} above the nearest $t_{2g}{}^3$ state. From this energy a relaxation via a configuration coordinate interaction to the $\Gamma_8(^2T_{2g})$ would be more probable eventually leading to population of the luminescent $\Gamma_7(^2T_{2g})$ level by additional multiphonon processes.

To our knowledge this constitutes the first observation of resolved sharp-line luminescence for a $5d$ ion. The observations are in excellent agreement with what could be expected based on the absorption measurements of Dorain and Wheeler. These suggest that sharp-line luminescence of the transition metals need not be restricted to elements of the first transition series but under appropriate conditions exist also for the $4d$ and $5d$ elements. Additional work along these lines is proceeding.

The original suggestion that the $5d$ ions might show sharp-line luminescence was made by M. de Wit to whom we are grateful for this as well as for his continuing interest and helpful criticisms. The authors benefited from many useful discussions with Dr. H. B. Bebb, Dr. R. K. Watts, and Dr. W. C. Holton. E. Ruthven and J. Pinnell are acknowledged for their assistance in preparing the crystals.

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Field-Emission Studies of Electronic Energy Levels of Adsorbed Atoms

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The relative changes in the total energy distribution of field-emitted electrons upon adsorption of single atoms have been measured for adsorption of the alkaline-earth atoms (Ba, Sr, and Ca) on several crystal planes of tungsten. The expected perturbations of the energy distribution due to the tunneling resonance through an atomic "virtual level" at various positions relative to the Fermi surface and of various half-widths Γ is demonstrated by a simple one-dimensional calculation. The measured energy-dependent structure in the current-enhancement factor due to the adsorbate has been interpreted in a tunneling-resonance model to yield the positions and shapes of the atomic "virtual levels." The ground-state ^1S $6s^2$ level of Ba is broadened to a half-width $\Gamma_S = 0.75$ eV and shifted upward by $\Delta E^S = 0.95$ eV. This causes it to overlap and mix with the first two excited states: a triplet ^3D $6s5d$ and a singlet ^1D $6s5d$. The observed ^3D and ^1D levels were not shifted and had a half-width $\Gamma_D = 0.1$ eV. Similarly, the first excited state of Ca, a triplet ^3P $4s4p$, was shifted by $\Delta E^{3P} \approx 0.4$ eV with a width $\Gamma_{3P} \approx 0.3$ eV ($2\Gamma = \text{FWHM}$). The effect of the band structure of the substrate on tunneling resonance is discussed.

I. INTRODUCTION

The present knowledge of the interaction of atoms with surfaces has evolved from thermodynamic interpretation of a variety of experiments on increasingly clean and well-characterized surfaces. A rather recent shift to new and more sensitive experiments coupled with a spurt of quantum-theoretical calculations has signaled a turn toward quantum-mechanically oriented surface science. Furthermore, experimental techniques are now being developed and used which measure directly the quantum behavior of surfaces and adsorbate-surface interactions. In conjunction with recent theoretical studies, these experiments are expected to cast a new light on the fundamental behavior of surfaces and surface-atom interactions.

The scope of these experiments is evident from the examples which follow. Molecular vibrational levels of

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