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# Sharp-Line Luminescence from $Os^{4+}$ and $Mo^{3+}$ in $Cs_2HfCl_6$ †

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Sharp-line luminescence spectra have been obtained for $Os^{4+}$ ($5d^4$) and $Mo^{3+}$ ($4d^3$) in single cubic crystals of $Cs_2HfCl_6$. For $Os^{4+}$, luminescence from both the $^1E(\Gamma_3)$ and $^1T(\Gamma_5)$ levels of the $t^4$ configuration to all the spin-orbit split levels of the $^3T_1$ ground state are observed. Luminescence spectra from the $^2E$ ("R" lines) of $Mo^{3+}$ are reported for the first time. Sharp vibronic lines are observed in the vicinity of 1.1 $\mu$ due to coupling with odd-mode vibrations of the nearest-neighbor complex. Excitation spectra reveal pumping due to absorption into the $^4T_2$ and $^4T_1$ bands at $23.0 \times 10^3$ cm$^{-1}$ and $19.5 \times 10^3$ cm$^{-1}$, respectively, and to the $^2T$ level at $14.0 \times 10^3$ cm$^{-1}$. The excitation bands do not correlate with the major absorption bands observed in these crystals, suggesting that other charge states of molybdenum are simultaneously present in the crystals.

## I. INTRODUCTION

Compared to the large amount of information commonly available concerning the luminescent properties of the first transition-metal series, there is a general paucity of luminescence data for the second and third transition-metal series of ions as impurities in solids. Indeed, except for the notable work of Dorain and his co-workers,[1-3] there has been little detailed spectroscopy of any kind of the $4d$ and $5d$ ions as impurities in solids. Much of the prior work is concerned with the aqueous chemistry of complexes of these materials and hence consists primarily of absorption spectra. In a previous publication we described the sharp-line luminescence of $Re^{+4}(5d^4)^4$ in cubic single crystals of $Cs_2ZrCl_6$ and $Cs_2HfCl_6$ in the vicinity of 7000 Å. In this paper we report on the infrared luminescence of $Os^{4+}$ ($5d^4$) and on the observation of "R"-line luminescence of $Mo^{3+}$ ($4d^3$).[5] From the luminescence of $Os^{4+}$ in $Cs_2HfCl_6$, we determine the energy of the lowest excited levels of the $^3T_1$ ground state. This level is split by a combination of the cubic field and the large spin-orbit coupling. The energies of these states have been calculated by Dorain, Patterson, and Jordan[2] but have not been verified by direct experimental observation.

To our knowledge, the spectrum of the $R$-line luminescence of $Mo^{+3}$ has not been previously reported, although its excitation spectrum in glasses has been described elsewhere.[6]

## II. EXPERIMENTAL

Although crystals of $Cs_2HfCl_6$ were grown by techniques described previously,[4] sufficient difficulty was encountered in producing good single crystals that a more detailed description of the process is warranted. In addition, there may be some question as to the charge state of the molybdenum impurity in similarly prepared material making the details worthwhile reporting. For reasons which we were unable to ascertain, considerably more success was had in preparing the hafnium salts over those containing zirconium. For that reason the data reported here were all taken with $Cs_2HfCl_6$. We believe that the results reported here are not peculiar to the hafnium compounds although they may not extend to such related compounds as $K_2SnCl_6$.
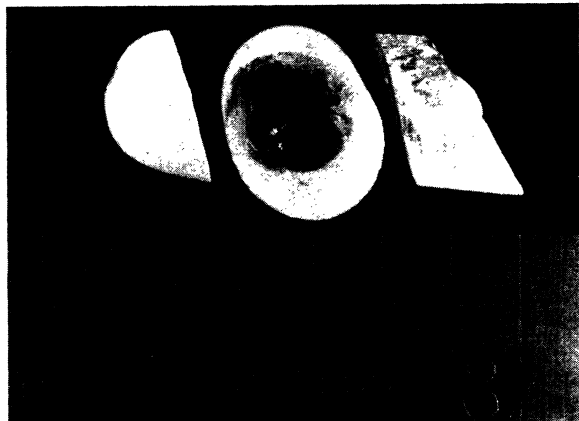
FIG. 1. Single-crystal sample of Bridgeman grown
$Cs_2HfCl_6$ .

Starting material for crystal growth was prepared
essentially in the manner described previously.[7,8]
It was found, however, that good crystals could not
be grown unless the initial powder was first care-
fully vacuum sublimed and then slowly melted in a
chlorine atmosphere. The pressure of the chlorine
was regulated to produce a clear colorless melt.
Usually several hundred Torr were required. After
cooling, the quartz tubes containing the material
were evacuated and the material was sublimed a
second time, slowly enough to drive off any excess
chlorine. The tube was then sealed off under vac-
uum. Further operations were performed in a dry
box. Impurities in the desired concentration were
then added to the undoped crystals usually in the
form of chlorides, $K_2ReCl_6$, $K_2OsCl_6$, and $MoCl_5$.
This was done in the dry box in as short a time as
possible. The ampoule was quickly reevacuated
and sealed off. The final crystal growth was per-
formed by dropping the ampoule through a vertical
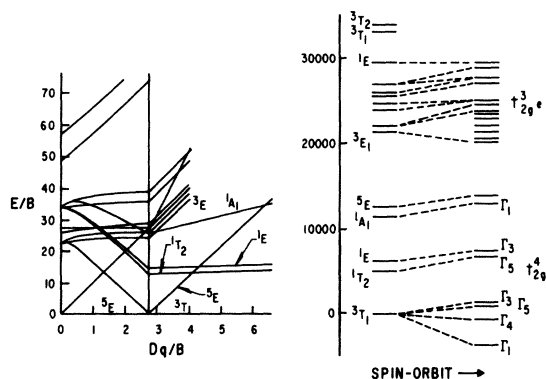Bridgeman furnace at between 1 and 2 mm/h. The



FIG. 3. Total low-resolution luminescence spectrum
for $Os^{4+}$ in $Cs_2HfCl_6$ at 2 °K.

crystals were allowed to anneal at 500 °C for sev-
eral hours before the furnace was turned off and
allowed to cool slowly to room temperature. Un-
less this procedure was followed, the crystals
were usually very severely cored with only an out-
side shell that was useful for optical measurements.
A typical example of a good crystal is shown in
Fig. 1.

Luminescence and absorption data were taken
with standard equipment described previously.[4]
The samples were either immersed in the appro-
priate cryogenic fluid or in an inert atmosphere in
order to prevent attack by moisture.

### III. EXPERIMENTAL RESULTS

#### A. $Os^{4+}$

The energy levels of $Os^{4+}$ in cubic crystals in-
cluding $Cs_2HfCl_6$ have been analyzed in great de-
tail by DPJ from low-temperature absorption spec-
tra. The luminescence which we have observed is
most readily understood with reference to their
energy-level diagram which we have reproduced
for convenience in Fig. 2. We have also included
for reference the Tanabe-Sugano diagram for the
$d^4$ configuration. In Fig. 3 we show the over-all
luminescence spectrum observed under low resolu-
tion at 2 °K. The relatively weak line at 16 910



FIG. 2. Energy-levels diagram for (a) $d^4$ configura-
tion in a cubic octahedral field (after Tanabe and Sugano),
and (b) $Os^{4+}(d^4)$ including the effects of a large spin-orbit
interaction (from DPJ, Ref. 2).



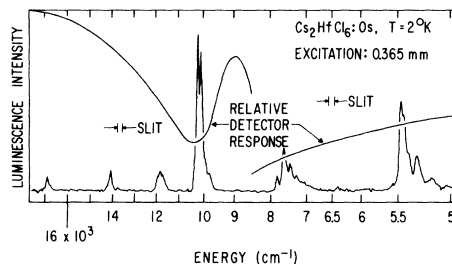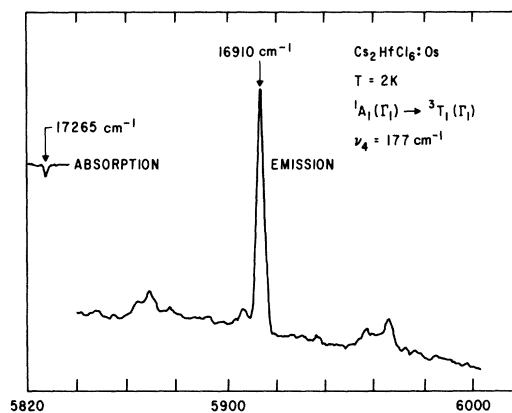FIG. 4. Spectrum of highest-energy luminescent
transition of $Os^{4+}$ in $Cs_2HfCl_6$.

$cm^{-1}$ is readily assigned using the results of DPJ as being due to a transition from the $^1A_1(\Gamma_1)$ to the $^3T_1(\Gamma_1)$ ground state. This line is also seen in absorption and a high-resolution spectrum is shown in Fig. 4. The absorption at $17\,265$ $cm^{-1}$ compares very well to that observed for $Os^{4+}$ in $Cs_2ZrCl_6$ by DPJ at $17\,252$ $cm^{-1}$ and assigned by them to coupling of the $\nu_4$ vibration with the nominally forbidden $d$-$d$ transition within the $t_4$ manifold. If we assign the strong emission line at $16\,910$ $cm^{-1}$ as the mirror image of the vibronic coupled absorption, we obtain a value for $\nu_4$ of $177$ $cm^{-1}$. This is identical to the value found for this vibration in $Cs_2OsCl_6$ from infrared spectra by Woodward and Ware. [9] The corresponding value for $Re^{4+}$ in $Cs_2HfCl_6$ is $173$ $cm^{-1}$. The weaker lines shown in Fig. 4 are most probably due to other odd-mode vibrations of the $OsCl_6^{2-}$ complex. The highest energy line at $17\,036$ $cm^{-1}$ is tentatively identified as a $\nu_7$ vibration while the lowest energy line at $16\,759$ $cm^{-1}$ is believed to be a $\nu_3$ vibration. From the position of the $\nu_4$ absorption and emission lines we predict that the zero phonon line would occur at $17\,088$ $cm^{-1}$. This line is not observed in emission. It was also not observed in absorption by DPJ in $Cs_2ZrCl_6$, although a weak zero phonon line was seen in $K_2PtCl_6$. All transitions in the zirconate were weaker and broader than the corresponding transitions in the platinate.

Returning to an anlysis of the lower energy transitions shown in Fig. 3 we interpret the lines near $14\,000$ and $12\,000$ $cm^{-1}$ to be due to transitions from $^1A_1(\Gamma_1)$ to the $^3T_1(\Gamma_4)$ and $^3T_1(\Gamma_5, \Gamma_3)$, respectively. Similarly, the strong group of lines near $10\,000$ $cm^{-1}$ is from the $^1T_2(\Gamma_5)$ to the $\Gamma_1$ ground state while the groups at $7600$ $cm^{-1}$ and $5500$ $cm^{-1}$ are to the split-off ground levels $^3T_1(\Gamma_4)$ and $^3T_1(\Gamma_5, \Gamma_3)$. From these two sets of transitions we calculate the energy levels of the lowest-lying excited states of the spin-orbit split $^3T_1$. The results are shown in Table I together with the calculated positions. [10] A considerable amount of structure, presumably

TABLE I. Lowest-energy excited states of $^3T_1$ ground state of $Os^{4+}$ in $Cs_2HfCl_6$.

| | Level | | |
|---|---|---|---|
| | $\Gamma_4$ | $\Gamma_5$ | $\Gamma_3$ |
| Luminescence from $^1A_1$ | 2820 | (5070)[a] | |
| Luminescence from $^1T_2$ | 2729 | 4765 | 4942 |
| Calculated[b] | 2853 | 4628 | 4896 |

[a]$\Gamma_5$ and $\Gamma_3$ are unresolved; value shown is average position.

[b]Unpublished results of Dorain, Patterson, and Jordan, Ref. 2.

vibronic, is observed in the lowest-energy lines. We have, however, been unable to assign these to any specific odd-mode vibrations.

### B. $Mo^{3+}$

The absorption spectra of $Mo^{3+}(4d^3)$ in aqueous solution as well as the reflection spectrum of solid $K_3MoCl_6$ have been reported by Hartmann and Schmidt[11] and further analyzed by Runciman and Schroeder. [12] Including spin-orbit interaction, they find that the $^2E$ level should be at $9167$ $cm^{-1}$. This level, which is responsible for the $R$-line luminescence of $Cr^{3+}(3d^3)$, has not been previously observed in fluorescence for the corresponding $4d^3Mo^{3+}$ ion. Weak absorptions for several molybdenum compounds between $8800$ and $9800$ $cm^{-1}$ are assigned to the $^4A_g \rightarrow {}^2E_g$, $^2T_g$ transition by Purlani and Piovesana. [13] Watson and Parke[6] report on the excitation spectrum of an approximately $1$-$\mu$ fluorescence of $Mo^{3+}$ in glass, determining the positions of the spin-allowed $^4T$ levels, but do not show the actual luminescence spectrum. We have, in fact, been unable to find any previous report of the luminescence spectrum of this ion.

When crystals of $Cs_2HfCl_6$ containing approximately 1% (starting) by weight of $MoCl_5$ are excited at room temperature by a strong Hg arc, we observe a relatively intense double-peaked luminescence in the vicinity of $1.0$ $\mu$. As the temperature of the crystal is lowered, the luminescence lines narrow, split up, and change in intensity as shown in Fig. 5. The mirror symmetry which is most easily seen at temperatures below about $150\,°K$ and the disappearance of the high-energy components at liquid-helium temperature clearly establishes the vibronic nature of the transition.

Since it is not obvious that $Mo^{+3}$ will substitute uncompensated in a four-valent site, attempts were made to obtain further substantiating evidence concerning the charge state of the impurity. The strongest evidence is, of course, the location of the sharp luminescence peak which fits the predicted position of the $^2E$ level of the $d^3$ configuration rather well. Sharp lines could also arise from the $^1A$ and $^1E$, $^1T_2$ levels of $d^2$ but these would occur near $16\,000$ and $6500$ $cm^{-1}$, respectively. [14] Broad strong absorption bands centered at $24\,500$ $cm^{-1}$ and $28\,170$ $cm^{-1}$ were at first believed to be the $^4T_2$ and $^4T_1$, respectively. [5] There is, however, no evidence of absorption into the $^2T_{2g}$ level near $15\,000$ $cm^{-1}$ as has been reported for other molybdenum-containing compounds. [13] Also, the spin-allowed bands in $K_3MoCl_6$ were reported to occur at $19\,400$ and $24\,200$ $cm^{-1}$, respectively, approximately $5000$ $cm^{-1}$ lower in energy than the bands observed in our crystals. Spin-allowed transitions to the $^4T$ levels have been reported, however, at $21\,000$ and $25\,800$ $cm^{-1}$ for what is believed to be $MoOCl_5^{4-}$. [13]
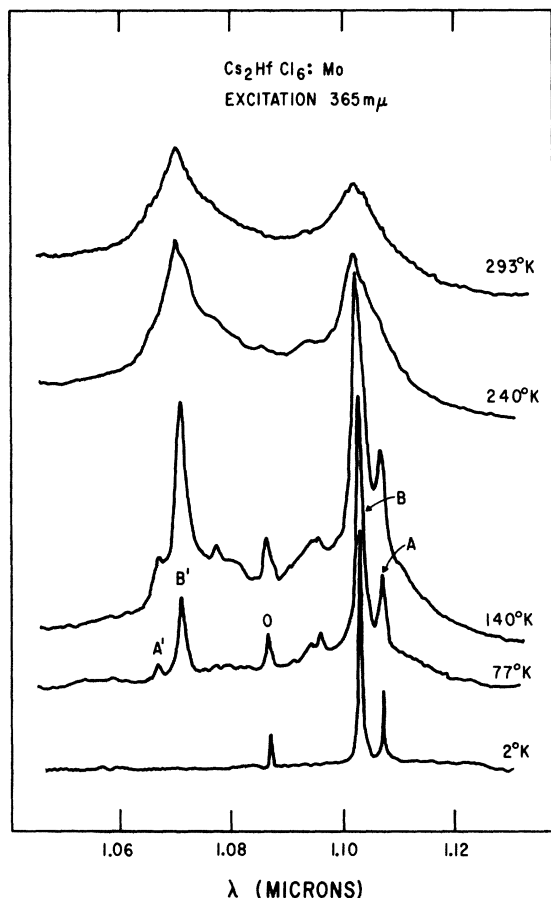
FIG. 5. Luminescence spectrum of $Mo^{3+}$ in $CsHfCl_6$.

To determine if the observed absorption spectra is connected to the same impurity that gives rise to the luminescence, we have obtained a low-resolution excitation spectrum. This is shown in Fig. 6. We observe a weak peak at $14.0 \times 10^3$ cm$^{-1}$ and a stronger one at $19.5 \times 10^3$ cm$^{-1}$ as well as a shoulder near $23.0 \times 10^3$ cm$^{-1}$. These are obviously the $^2T$, $^4T_2$, and $^4T_1$ levels, respectively. The main absorption spectrum that we observe is, then, either some other charge state of molybdenum or possibly charge-transfer bands. Most likely the excitation bands are not seen in absorption because of a combination of low concentration and severe broadening due to strains and possibly a variety of environments. We are unable to eliminate the possibility of some type of oxychloride complex since many of these are known to exist.

Attempts to verify the charge state and local symmetry of the Mo impurity by spin-resonance measurements have not yielded convincing data. Low[15] reports observing EPR due to $Mo^{+5}$ in $K_2SnCl_6$. He observes three equivalent anisotropic spectra each with tetragonal symmetry along one of the cube axes apparently due to charge compensation. We

observe a complex EPR spectrum whose strongest component appears to be isotropic with $g = 1.97$. Low observed $g_{11} = 1.974$ in $K_2SnCl_6$. Identical $g$ values have been reported for both pure $K_3MoCl_6$ and the oxychloride,[16] making this mode of identification suspect unless the chemical nature of the material is very well defined. As is the case with the absorption spectrum, correlating the EPR line with the luminescence line is unwarranted.

Additional evidence for $Mo^{+3}$ is obtained from a measurement of the luminescence lifetime. This was determined to be essentially constant at 9.5 msec between 300 and 77 °K, which is a reasonable value for the $^2E$-$^4A$ transition of the $d^3$ configuration. We believe that the best evidence for the presence of $Mo^{+3}$ is the luminescence spectrum and its associated excitation bands.

As with other $d$-$d$ transitions that arise between states of the same $t^n$ configuration, coupling of the electronic levels with odd-mode vibrations of the crystal lattice increases the transition probability. The low-temperature luminescence spectrum provides a convenient method of identifying these vibrations. In this case the vibrations are characteristic of the ground state of the ion which for transitions within a given $t^n$ manifold are essentially identical to those in the excited state. Referring to the bottom curve in Fig. 5, we identify a zero phonon line at 9201 cm$^{-1}$ with two easily observed phonon side bands. They are separated from the zero phonon by a strong line at 137 cm$^{-1}$ and a weaker one at 171 cm$^{-1}$. If the stronger line is assigned to the $\nu_4$ odd stretching vibration of the $MoCl_6^{3-}$ cluster, then it is about 50 cm$^{-1}$ less than what has been measured for this vibration of $Ru^{+4}$ in $K_2RuCl_6$ and 40 cm$^{-1}$ less than has been assigned to the $\nu_4$ vibration of $Ru^{+4}$ in $K_2PtCl_6$.[3] A decrease
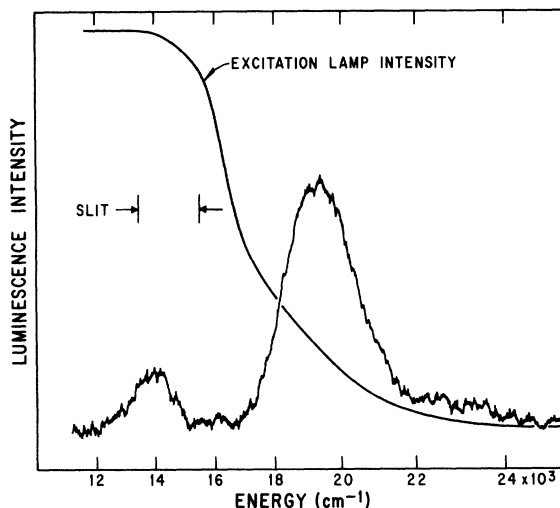


FIG. 6. Excitation spectrum for the 1-$\mu$ luminescence of $Mo^{3+}$.

TABLE II. Energy and identification at 77 °K of $Mo^{+3}$ luminescence lines $^2E \rightarrow {}^4A$ transition.

| Line[a] | Energy (cm$^{-1}$) | Description | Energy separation from 0 |
|---|---|---|---|
| A | 9030 | $0 - b_1(\nu_4)$ | - 171 |
| B | 9064 | $0 - e(\nu_4)$ | - 137 |
| 0 | 9201 | 0 phonon | 0 |
| B' | 9334 | $0 + e(\nu_4)$ | + 133 |
| A' | 9371 | $0 + b_1(\nu_4)$ | + 170 |

[a]Line references refer to Fig. 5.

of this amount for the trivalent charged ion in a normally +4 site is consistent with what has been observed for different charge states of iridium in $K_2IrCl_6$.[17] Assigning the stronger line to $\nu_4$, however, makes the assignment of the weaker line difficult. The $\nu_6$ vibration which is determined to be 108 cm$^{-1}$ for $Ru^{+4}$ is expected in any case to be smaller than the $\nu_4$ while the $\nu_3$ at 346 cm$^{-1}$ is too large. There are no other simple odd modes for the $MoCl_6$ complex. Since, as mentioned above, the presence of oxychloride complexes cannot be excluded, this may also be the explanation for the apparent discrepancy in the value of the vibrational energies. An oxygen ion replacing one of the chlorines in the $MoCl_6$ structure results in a tetragonal distortion of the cubic field. The $\nu_4$ vibration which has $t_{1u}$ symmetry will split into a $b_{1u}$ and an $e_u$ vibration, both of which will couple strongly with the electronic level. Additional lines that appear between the zero phonon line and the strong line (these are most easily seen in the 77 °K data) may be due to lattice phonons and possibly the $\nu_6$ vibration. At higher temperatures the anti-Stokes luminescence on the high-energy side of the zero phonon line are clearly visible. The most prominent transitions are listed in Table II along with their tentative identification as outlined above. The difference in the phonon energy between the Stokes and anti-Stokes lines shown in the last column to

the right in the table is not experimentally significant. At even higher temperature the lines broaden so that at 240 °K and above only a double-humped spectrum is observed. The apparent increase in intensity of the anti-Stokes line over the Stokes line is an artifact due to the rapid change in sensitivity of the S-1 photomultiplier over the separation of the peaks. This amounts to a decrease of approximately 1.5 times between 1.07 and 1.1 $\mu$. We have attempted to obtain a rough estimate of the quantum efficiency for the $Mo^{+3}$ luminescence by comparing it with the luminescence of a piece of lightly doped ruby. We obtain a value of 14% which, considering the possibility of several types of molybdenum being present in the crystal, suggests that the intrinsic efficiency is considerably higher.

## IV. CONCLUSIONS

As previously reported for $Re^{4+}$ ($5d^3$), $Os^{4+}$ ($5d^4$) also shows sharp-line luminescence from states that have the same strong field configuration as the ground level. Identification of these levels is made by comparison with the results of DPJ. $Mo^{3+}$ ($4d^3$) exhibits $R$-line luminescence similar to $Cr^{3+}$ ($3d^3$) but with sharp vibronic bands due to odd-mode coupling with the electronic levels. Additional types of molybdenum ions other than the trivalent charge state make interpretation of the absorption and EPR spectra uncertain.

## ACKNOWLEDGMENTS

†Research sponsored in part by the U. S. Air Force Office of Scientific Research under Contract No. F44620-67-C-0073.

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# Pseudopotential Calculation of Knight-Shift Temperature and Volume Dependence in Liquid and Solid Sodium[†]

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We have used a pseudopotential formalism to compute the electron density at a nuclear site in liquid and bcc solid sodium. The temperature dependence of the electron density at atmospheric pressure is found to account satisfactorily for the experimental observation that the sodium Knight shift increases with temperature. A decrease would be expected to accompany lattice expansion in a free-electron metal. In addition, the temperature dependence at constant volume and the pressure dependence of the electron density are computed and compared with published experimental data. Agreement between theory and experiment is rather better for the liquid state than for the solid, probably because of a less than satisfactory approximation to the high-temperature solid lattice structure.

## INTRODUCTION

The Knight shift of a simple metal is given by[1]

$$K = \tfrac{8}{3}\pi \chi \, \Omega \, P_F , \tag{1}$$

where $\chi$ is the dimensionless-spin susceptibility, $\Omega$ is the volume, and the "penetration factor" $P_F$ is the average probability density for Fermi-energy electrons at a nucleus. Interactions other than the above contact term are expected to contribute no more than roughly 10% to the Knight shift of light nonmagnetic metals and are neglected in this paper. For free electrons, $\Omega P_F$ is unity; the spin susceptibility and, consequently, the Knight shift are proportional to the inverse cube root of the volume. Both should increase under pressure, and since the explicit dependence on temperature is usually negligible compared with the implicit dependence through lattice expansion, both should decrease with rising temperature. For real metals the volume and temperature dependence of $\Omega P_F$ must be considered as well. For example, the Knight shift of sodium is found to increase with temperature and decrease under pressure,[2-4] exactly the opposite of free-electron behavior. Although the spin susceptibility of sodium has not been measured with sufficient accuracy to determine its temperature or volume dependence, it has been shown theoretically[5] that within a given phase the volume dependence of $\chi$ is essentially free-electron-like. The different volume and temperature dependences of $K$ and $\chi$ are attributed to changes in $\Omega P_F$.

There have been a number of previous calculations of the magnitude and volume dependence of the sodium-penetration factor at zero temperature.[6-12]

No prior work on the temperature dependence for sodium has been done, but Halder[13] has recently considered the effect of temperature on polyvalent liquid-metal Knight shifts in a manner similar to our treatment and Kasowski[14] has reported an elegant calculation of the anomalous temperature dependence of the solid-cadmium Knight shift. We have used the pseudopotential method to calculate the penetration factor vs temperature for bcc solid sodium and liquid sodium at normal pressure and for liquid sodium at constant volume. In addition, the volume dependence for solid sodium at room temperature was found. In order to obtain the Knight shift from Eq. (1) we assume that $\chi$ has a free-electron volume dependence, has no explicit temperature dependence, and is normalized to the experimental value[15] of $1.13 \times 10^{-6}$ at room temperature and pressure. Results are shown in Figs. 1 and 2.

## THEORY AND RESULTS

It is relatively straightforward to find the perturbation of electron-wave functions by the pseudopotential.[16] One takes as zero-order states the orthogonalized-plane-wave (OPW) wave functions

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{(\alpha\Omega)^{1/2}}\left[ e^{i\vec{k}\cdot\vec{r}} - \sum_{j,n} A_j(\vec{k})\, e^{i\vec{k}\cdot\vec{R}_n}\, \varphi_j(\vec{r} - \vec{R}_n)\right], \tag{2}$$

where $\varphi_j(\vec{r} - \vec{R}_n)$ is the $j$th core state of the ion at $\vec{R}_n$,

$$A_j(\vec{k}) = \int d^3 r\, \varphi_j^*(\vec{r})\, e^{i\vec{k}\cdot\vec{r}},$$

and

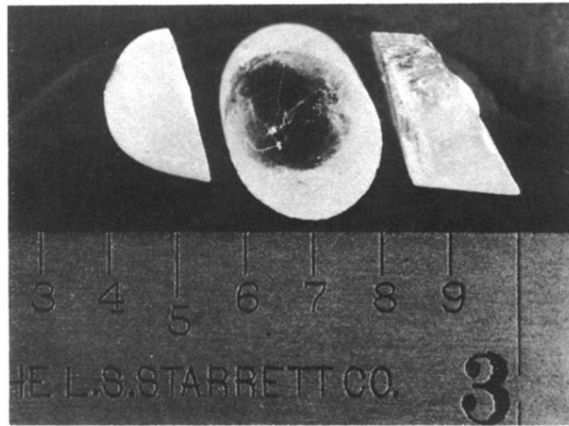$$\alpha = 1 - \frac{1}{\Omega} \sum_{j,n} |A_j(\vec{k})|^2 .$$

FIG. 1. Single-crystal sample of Bridgeman grown
$Cs_2HfCl_6$ .