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PHYSICAL REVIEW B

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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 $23.0 \times 10^3\ \text{cm}^{-1}$ and $19.5 \times 10^3\ \text{cm}^{-1}$, respectively, and to the 2T level at $14.0 \times 10^3\ \text{cm}^{-1}$. 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+} ($5d^4$) in cubic single crystals of Cs_2ZrCl_6 and Cs_2HfCl_6 in the vicinity of $7000\ \text{\AA}$. 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 Jordan² 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 .

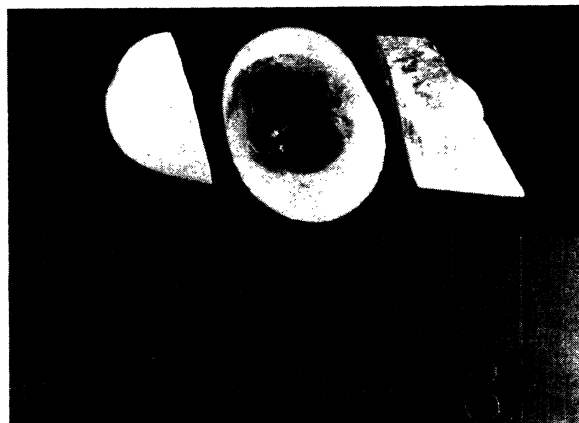


FIG. 1. Single-crystal sample of Bridgeman grown Cs_2HfCl_6 .

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 carefully 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 vacuum. 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 performed by dropping the ampoule through a vertical Bridgeman furnace at between 1 and 2 mm/h. The

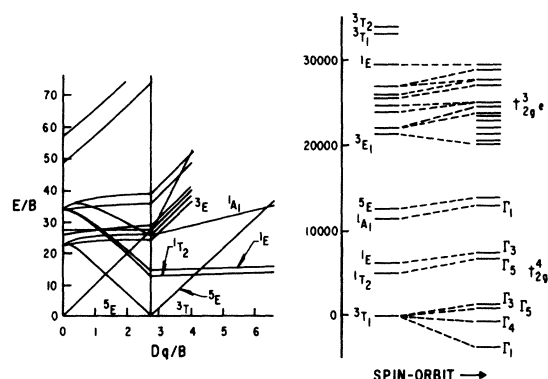


FIG. 2. Energy-levels diagram for (a) d^4 configuration in a cubic octahedral field (after Tanabe and Sugano), and (b) $\text{Os}^{4+}(d^4)$ including the effects of a large spin-orbit interaction (from DPJ, Ref. 2).

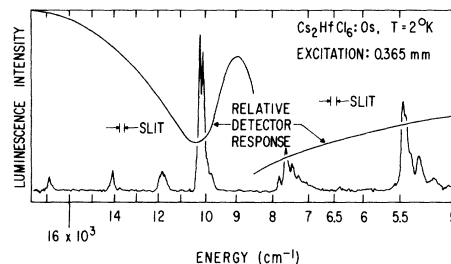


FIG. 3. Total low-resolution luminescence spectrum for Os^{4+} in Cs_2HfCl_6 at 2 °K.

crystals were allowed to anneal at 500 °C for several hours before the furnace was turned off and allowed to cool slowly to room temperature. Unless this procedure was followed, the crystals were usually very severely cored with only an outside 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 appropriate 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 including Cs_2HfCl_6 have been analyzed in great detail by DPJ from low-temperature absorption spectra. 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 resolution at 2 °K. The relatively weak line at 16910

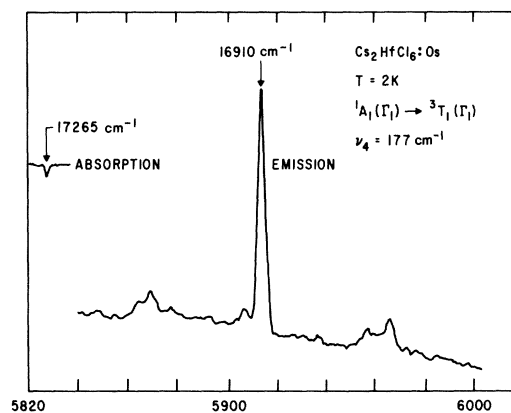


FIG. 4. Spectrum of highest-energy luminescent transition of Os^{4+} in Cs_2HfCl_6 .

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 17265 cm^{-1} compares very well to that observed for Os^{4+} in Cs_2ZrCl_6 by DPJ at 17252 cm^{-1} and assigned by them to coupling of the ν_4 vibration with the nominally forbidden $d-d$ transition within the t_4 manifold. If we assign the strong emission line at 16910 cm^{-1} as the mirror image of the vibronic coupled absorption, we obtain a value for ν_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 17036 cm^{-1} is tentatively identified as a ν_7 vibration while the lowest energy line at 16759 cm^{-1} is believed to be a ν_3 vibration. From the position of the ν_4 absorption and emission lines we predict that the zero phonon line would occur at 17088 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 analysis of the lower energy transitions shown in Fig. 3 we interpret the lines near 14000 and 12000 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 10000 cm^{-1} is from the $^1T_2(\Gamma_5)$ to the Γ_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

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 $\text{Mo}^{3+}(4d^3)$ in aqueous solution as well as the reflection spectrum of solid K_3MoCl_6 have been reported by Hartmann and Schmidt¹¹ 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 $\text{Cr}^{3+}(3d^3)$, has not been previously observed in fluorescence for the corresponding $4d^3\text{Mo}^{3+}$ 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 Piovessana.¹³ Watson and Parke⁶ report on the excitation spectrum of an approximately $1\text{-}\mu$ 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 1.0μ . 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 16000 and 6500 cm^{-1} , respectively.¹⁴ Broad strong absorption bands centered at 24500 cm^{-1} and 28170 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 15000 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 19400 and 24200 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 21000 and 25800 cm^{-1} for what is believed to be MoOCl_5^{4-} .¹³

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

	Level		
	Γ_4	Γ_5	Γ_3
Luminescence from 1A_1	2820	(5070) ^a	
Luminescence from 1T_2	2729	4765	4942
Calculated ^b	2853	4628	4896

^a Γ_5 and Γ_3 are unresolved; value shown is average position.

^bUnpublished results of Dorain, Patterson, and Jordan, Ref. 2.

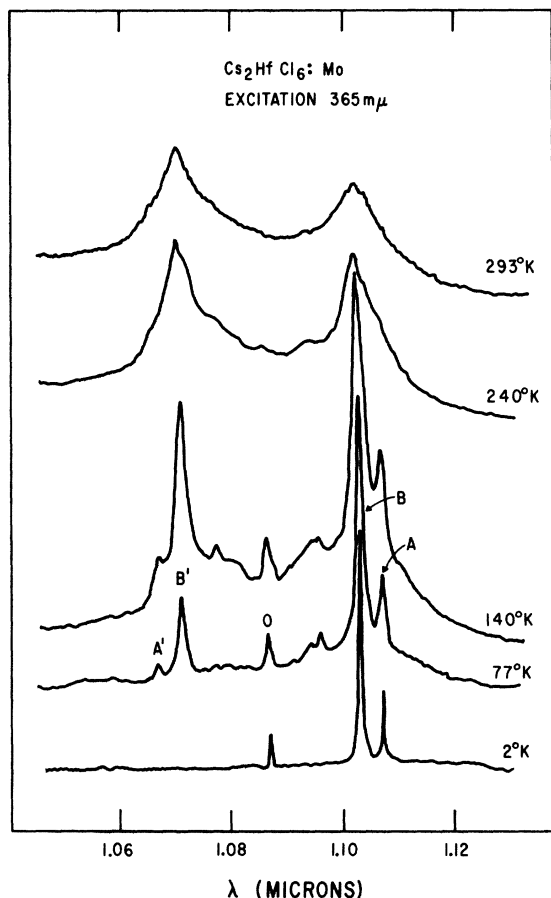


FIG. 5. Luminescence spectrum of Mo^{3+} in CsHfCl_6 .

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 $14.0 \times 10^3 \text{ cm}^{-1}$ and a stronger one at $19.5 \times 10^3 \text{ cm}^{-1}$ as well as a shoulder near $23.0 \times 10^3 \text{ cm}^{-1}$. These are obviously the 2T_1 , 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. Low¹⁵ 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 $^2E \rightarrow ^4A$ 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 ν_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 ν_4 vibration of Ru^{4+} in K_2PtCl_6 .³ A decrease

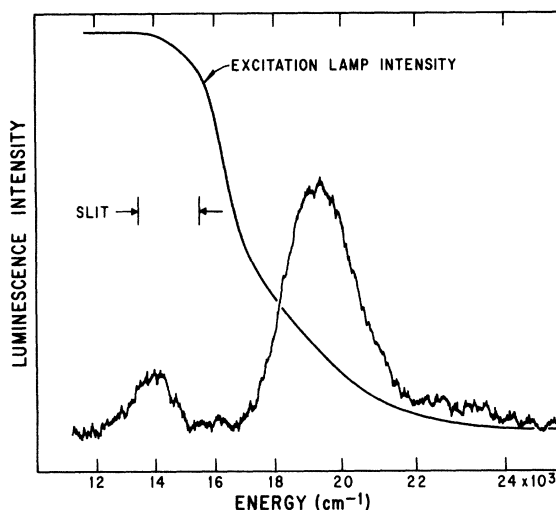


FIG. 6. Excitation spectrum for the $1\text{-}\mu$ luminescence of Mo^{3+} .

TABLE II. Energy and identification at 77 °K of Mo³⁺ luminescence lines ²E → ⁴A transition.

Line ^a	Energy (cm ⁻¹)	Description	Energy separation from 0
A	9030	0 - b ₁ (ν ₄)	- 171
B	9064	0 - e(ν ₄)	- 137
0	9201	0 phonon	0
B'	9334	0 + e(ν ₄)	+ 133
A'	9371	0 + b ₁ (ν ₄)	+ 170

^aLine 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 K₂IrCl₆.¹⁷ Assigning the stronger line to ν₄, however, makes the assignment of the weaker line difficult. The ν₆ vibration which is determined to be 108 cm⁻¹ for Ru⁴⁺ is expected in any case to be smaller than the ν₄ while the ν₃ at 346 cm⁻¹ is too large. There are no other simple odd modes for the MoCl₆ 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 MoCl₆ structure results in a tetragonal distortion of the cubic field. The ν₄ 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 ν₆ 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 μ. We have attempted to obtain a rough estimate of the quantum efficiency for the Mo³⁺ 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 Re⁴⁺ (5d³), Os⁴⁺ (5d⁴) 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. Mo³⁺ (4d³) exhibits R-line luminescence similar to Cr³⁺ (3d³) 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.

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PHYSICAL REVIEW B

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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 by¹

$$K = \frac{8}{3} \pi \chi \Omega P_F, \quad (1)$$

where χ is the dimensionless-spin susceptibility, Ω 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, ΩP_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 ΩP_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 theoretically⁵ that within a given phase the volume dependence of χ is essentially free-electron-like. The different volume and temperature dependences of K and χ are attributed to changes in ΩP_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 Halder¹³ has recently considered the effect of temperature on polyvalent liquid-metal Knight shifts in a manner similar to our treatment and Kasowski¹⁴ 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 χ has a free-electron volume dependence, has no explicit temperature dependence, and is normalized to the experimental value¹⁵ of 1.13×10^{-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

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

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

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

and

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

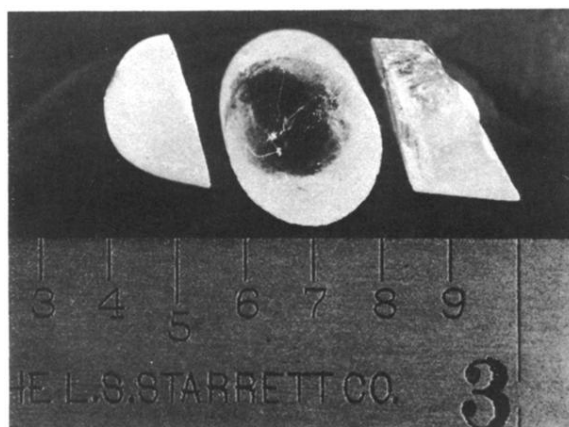


FIG. 1. Single-crystal sample of Bridgeman grown Cs_2HfCl_6 .