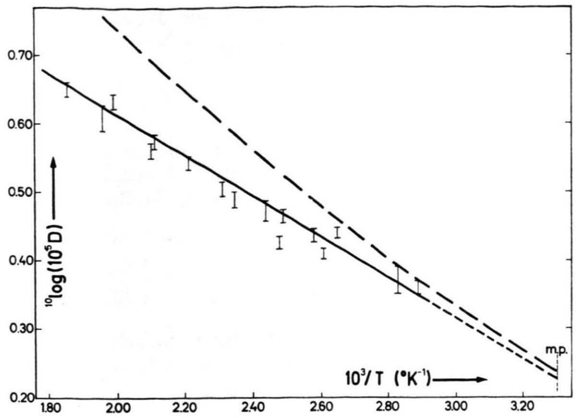

Fig. 1. Arrhenius plot of impurity diffusion of $^{115m}$In in liquid gallium. Dashed curve: Ga self-diffusion, Ref. [1].

(energy in kcal/mole) for the diffusion of tracer In in liquid Ga between 73° and 266 °C.

The effective "activation energy", 1.32 kcal/mole, is by about 0.6 kcal/mole lower than that for Ga self-diffusion in the same temperature range. The two Arrhenius plots are seen to converge and cross not far from the melting point of Ga. The marked departure from a straight line, exhibited by the self-diffusion data [2], is also suggested by the present results.

At higher temperature the ratio of self-diffusion to tracer diffusion is about 1.4, i. e. significantly higher than the root of the ratio, 1.6, of the tracer masses.

Only few investigations have hitherto been made of impurity diffusion in liquid metals. In the Ag matrix system, Leak and Swalin [5, 6] have found a nearly linear dependence of $\Delta Q$ (= the difference in "activation energy" between solute and solvent diffusion) on the excess valence $\Delta Z$ of the impurity. The homovalent impurity Au in Ag, which according to LeClaire [7] possesses an effective $\Delta Z$ of about $-0.9$, has been found by Gupta [6] to fit into the same systematics, $\Delta Q = -A \cdot \Delta Z$, where $A \cong 0.8$ kcal/mole. This is in agreement with arguments analogous to solid-state theory of impurity diffusion [7, 8], i. e. with the view that positive centers of charge should attract "free volume", as they attract vacancies in the solid metals. The analogy can be applied without giving preference to any particular model of liquid diffusion [6]. For the Ga matrix system, a similar treatment allows the qualitative prediction $A \approx 0.7$. Also according to Ref. [7], the excesss valency can be calculated for a homovalent impurity from

$$\Delta Z = \left[\Delta F + \frac{1}{n}\Delta H + \frac{1}{n}\Delta \Sigma I\right] B,$$

where the RHS denotes the solute-solvent difference in Fermi energy, in the heat of sublimation and in the sum of the $n$ ionization potentials. The factor $B$ is of the order $1.6 \cdot 10^{-2}$; for In in Ga $n=3$ and the parenthesis is about 60. Accordingly $\Delta Z \cong +1.0$, i. e. the In tracer in Ga behaves as effectively tetravalent. The analogy with the treatment of Ag-data [6] then leads to the prediction $\Delta Q \cong -0.7$, in good qualitative agreement with the observed $\Delta Q_{\text{exp}} \cong -0.6$.

In spite of the smaller "activation energy", the ratio $D_i/D_s$ (i for impurity-, s for self-diffusion) is less than unity throughout the range. Perhaps this may be connected with the great difference in mass between solute and solvent. However, the oposite behaviour is reported for Au in Ag; the heavy solute has the greater "activation energy" but diffuses faster than the solvent. A common feature for both cases is that $D_i/D_s$ is nearly unity at the melting point. Similar tendencies are seen in recent [9] measurements of the diffusion of $^{24}$Na in K and $^{42}$K in Na. The melting point cross-over may possibly be a clue to a further elaboration of liquid diffusion theory.

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# Vibrational Spectra and Force Constants of the Ions $^{92}MoO_4^{2-}$, $^{100}MoO_4^{2-}$, $^{92}MoS_4^{2-}$ and $^{100}MoS_4^{2-}$

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In the course of our systematic investigations of the spectroscopic properties of tetrahedral oxo-, thio- and seleno anions of transition metals with d$^0$ configuration, we have studied the internal vibrations of $MoO_4^{2-}$ and $MoS_4^{2-}$ from the infrared and Raman spectra of the salts $Na_2MoO_4$ and $K_2MoS_4$. It seemed to be interesting to see whether it is possible to calculate the exact values of the force constants using very heavy atom isotopic substitution data, because until now this problem has not been investigated.

The well known compounds were prepared on a milligram scale using the metal isotopes purchased from Oak Ridge National Laboratory. The purity of each metal isotope was: $^{92}$Mo (98.27%) and $^{100}$Mo (97.42%). The infrared spectra were measured on a Perkin-Elmer Model 325 spectrophotometer using the Nujol mull technique and the Raman spectra on a CODERG Raman spectrophotometer equipped with a He-Ne laser. The measured frequencies are given in Tables 1 and 2. The $\nu_3$ (Raman spectrum) and $\nu_4$ (infrared and Raman) frequencies show crystal field splittings. However the $\nu_3$ bands in the infrared spectra show very little splittings and hence they have been used to determine the isotopic shifts $\Delta\nu_3$ as additional data for the calculation of the force constants. The $\nu_4$ frequency values were taken from the aqueous Raman spectra of the substances containing natural abundance of molybdenum. Errors in the values of the force constants due to this approximation are negligible, since the force field is not sensitive to a small difference in the value of $\nu_4$. Further, the isotope shift in $\nu_4$ itself is very small and hard to measure accurately.

The following values of the symmetry force constants have been obtained, using the values of the frequencies and isotope shifts marked in Tables 1 and 2, by the well known method (for the definition of the $F$ matrix elements, see Ref. [1]).

$MoS_4^{2-}$: $F_{33}=2.84\pm0.12$, $F_{34}=-0.01\pm0.07$, $F_{44}=0.203\pm0.011$;
$MoO_4^{2-}$: $F_{33}=5.14\pm0.21$, $F_{34}=-0.22\pm0.21$, $F_{44}=0.38\pm0.03$.

Table 1. Vibrational frequencies of crystalline $Na_2MoO_4$ (cm$^{-1}$).

| | | $\tilde{\nu}$ (${}^{92}$Mo) | $\Delta\tilde{\nu}$ [a] | $\tilde{\nu}$ (${}^{95.9}$Mo) [b] | aq. soln. [b] |
|---|---|---|---|---|---|
| $\nu_1$ ($A_1$) | Raman | 890 (vs) | 0 | 890 (vs) | 897 (vs) |
| | Infrared | — | — | — | — |
| $\nu_3$ ($F_2$) | Raman | 811 (m) | 7 | 808 (m) | 841 (m) |
| | Infrared | 842 (s) [c] | 8 [c] | 838 (s) | — |
| $\nu_2$ (E) | Raman | 303 (s) [d] | 0 | 303 (s) [d] | 318 (s) |
| | Infrared | — | — | — | — |
| $\nu_4$ ($F_2$) | Raman | 381 (vw) [d] | 1—2 | 381 (vw) [d] | 318 (s) [c] |
| | Infrared | 317 (s) | 2 | 316 (s) | — |

[a] $\Delta\tilde{\nu}=\tilde{\nu}({}^{92}\mathrm{Mo})-\tilde{\nu}({}^{100}\mathrm{Mo})$.
[b] Natural isotope mixture.
[c] These frequencies were used for the calculations.
[d] The reverse assignment is also possible.

Table 2. Vibrational frequencies of crystalline $K_2MoS_4$ (cm$^{-1}$).

| | | $\tilde{\nu}$ (${}^{92}$Mo) | $\Delta\tilde{\nu}$ [a] | $\tilde{\nu}$ (${}^{95.9}$Mo) [b] | aq. soln. [b] |
|---|---|---|---|---|---|
| $\nu_1$ ($A_1$) | Raman | 456 (vs) | 1 | 456 (vs) | 458 (st) |
| | Infrared | 456 (w) | 1 | 456 (w) | — |
| $\nu_3$ ($F_2$) | Raman | 485 (m) | 5 | 482 (m) | |
| | | 477 (sh) | ~7 | ~475 (sh) | ~480 (sh) |
| | | 471 (s) | 5 | 469 (m) | |
| | Infrared | 478 (s) [c] | 7 [c] | 475 (s) | — |
| | | (477.9 [d]) | (6.8 [d]) | — | — |
| $\nu_2$ (E) and $\nu_4$ ($F_2$) [e] | | | | | |
| | Raman | 200 (w) | 1 | 199 (w) | 184 (m) [c] |
| | Raman | 180 (m) | 1 | 180 (m) | — |
| | Infrared | 203 (m) | 0 | 203 (m) | — |
| | Infrared | 188 (m) | 0 | 188 (m) | |

[a] $\Delta\tilde{\nu}=\tilde{\nu}({}^{92}\mathrm{Mo})-\tilde{\nu}({}^{100}\mathrm{Mo})$.
[b] Natural isotope mixture.
[c] These frequencies have been used in calculations.
[d] Average from five measurements.
[e] For assignment and discussion of the problem of distinguishing between $\nu_2$ and $\nu_4$ see ref. of A. MÜLLER, N. WEINSTOCK, and H. SCHULZE, Spectrochim. Acta (in press).

In these calculations, an error limit in the values of $\Delta\nu_3$ of $\pm0.5$ cm$^{-1}$ ($MoS_4^{2-}$) and $\pm1.0$ cm$^{-1}$ ($MoO_4^{2-}$) was assumed as a trial [2]. The values of the exact force constants calculated in our present study agree well with those obtained using different approximate methods [3–5]. It is expected that the application of these approximate methods yields good results for these ions, because the mass coupling is very small, which in turn implies that the coupling between $\nu_3$ and $\nu_4$ is very small [6–8].

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