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Formation of Thermal Vacancies on the Si Sublattice of the Intermetallic Compound MoSi$_2$


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For a detailed understanding of high-temperature processes in complex solids the identification of the sublattice on which thermal defects are formed is of basic interest. Theoretical studies in intermetallic compounds favor a particular sublattice for thermal vacancy formation. In the present study we detect in ordered MoSi$_2$ thermal vacancies with a low formation enthalpy of $H_f^\circ = (1.6 \pm 0.1)$ eV, and we succeed in showing by experimental and theoretical efforts that they are preferentially formed on the Si sublattice. By these data self-diffusion in MoSi$_2$ can be understood.

The positron annihilation lifetime spectra (time resolution 260 ps, $10^9$ coincidence counts) were analyzed by means of standard techniques [7]. The coincident measurements of the Doppler broadening of the annihilation photons with energies $E_1$ and $E_2$ were carried out by a collinear setup of two high-resolution Ge detectors with an energy resolution $\Delta E = 1.2$ keV. The high peak-to-background ratio ($>5 \times 10^5$) was achieved by diagonal cuts of the $(E_1, E_2)$-Doppler spectra along the $E_1 + E_2 = (1022 \pm 1)$ keV energy conservation line [13,18]. With the spectra of $>10^7$ coincidence counts we achieved good statistics in the region $E \approx (511 + 5)$ keV corresponding to $p_L \approx (19.6 \times 10^{-3})m_0c$ for the momenta of the chemically characteristic core electrons ($m_0$ is electron rest mass and $c$ is the velocity of light). The reference spectra of pure Mo and Si at ambient temperature were measured in a sandwich arrangement with a $^{22}$NaCl positron source. The $W$ parameter characterizes

![Diagram](https://example.com/diagram.png)

**FIG. 1.** Perfect and defected lattice structures of MoSi$_2$: (a) defect-free MoSi$_2$; (b) a vacancy located on the Si sublattice; (c) a vacancy located on the Mo sublattice.
For MoSi$_2$ at ambient temperature, which is confirmed by GGA calculations for delocalized positrons, demonstrates that structural vacancies in MoSi$_2$ at ambient temperature are negligible. This is concluded from the comparison of the positron lifetime $\tau$ and the valence electron density of MoSi$_2$, $\rho_\text{el} = 338$ nm$^{-3}$, with the corresponding values for pure metals and intermetallics [12].

For temperatures below 1050 K the free positron lifetime shows a weak temperature dependence (see Fig. 2) 

$$\tau_{\text{f}}(T) = \tau_{\text{f}0}(1 + \alpha T)$$

with the vacancy concentration

$$C_V(T) = \exp\left(\frac{E_V^f}{k_B T}\right) \exp\left(-\frac{H_V^f}{k_B T}\right).$$

Here, $\alpha$ is the temperature-independent specific positron trapping rate, $\tau_f$ is the positron lifetime in the defect-free crystal, $\tilde{\tau}$ is the mean positron lifetime, $H_V^f$ and $S_V^f$ are, respectively, the enthalpy and the entropy of vacancy formation, and $k_B$ is Boltzmann’s constant. The time constants $\tau_0 = [(1/\tau_f) + \sigma C_V]^\text{-1}$ and $\tau_1$ (characteristic for vacancies) as well as the relative intensities $I_0$ and $I_1$ can be deduced from the analyses of the positron lifetime spectra.

A fit of the temperature variation of the mean positron lifetime

$$\tilde{\tau}(T) = \frac{1 + \sigma \exp(S_V^f/k_B)}{1 + \sigma \exp(S_V^f/k_B)} \frac{1}{(\tau_f/\tau_1 - 1)}$$

derived from Eqs. (1) and (2) to the data in Fig. 2 taking into account the linear thermal expression $\tau_f(T)$ mentioned above, yields $H_V^f = (1.6 \pm 0.1)$ eV and $\sigma \exp(S_V^f/k_B) = (4.0 \pm 0.5) \times 10^{12}$ s$^{-1}$.

When a positron is trapped at a lattice vacancy the ratio of the annihilation probabilities with core or valence electrons is reduced compared to that of a positron delocalized on interstices as demonstrated by studies of vacancies in pure Si [23] and in pure Al [24]. Therefore, the temperature dependence of the Doppler broadening $W$ parameter (see Fig. 4) obtained from the high-momentum part of the electron momentum distribution of MoSi$_2$ (see Fig. 3) shows an S-shaped behavior in analogy to the positron lifetime measurements (Fig. 2) according to

$$W(T) = W_f \frac{1 + \sigma C_V W_1}{1 + \sigma C_V W_f}.$$

where $W_f$ and $W_1$ denote the $W$ parameters characteristic for the defect-free compound and for saturation trapping.
of positrons at thermal vacancies, respectively. A fit of Eq. (4) to the data in Fig. 4 yields the value of the vacancy formation enthalpy $H^F_V = (1.7 \pm 0.1)$ eV similar to the value derived from the positron lifetime studies.

Normalizing the vacancy formation enthalpy found in MoSi$_2$, to the melting temperature $T_M$ of the MoSi$_2$ yields a relatively low value $H^F_V/k_BT_M = 8.0$ similar to the low values $H^F_V/k_BT_M = 7.0$ to 9.5 reported for open-structured bcc-type intermetallic compounds [7,25] with high concentrations of thermal vacancies. This directly demonstrates the formation of high concentrations of thermal vacancies in MoSi$_2$.

For identifying the sublattice of MoSi$_2$ on which thermal vacancies are formed, measurements of the coincident Doppler broadening at 1343 K (see Fig. 5) are employed. At this temperature the majority of the positrons is annihilated in thermally formed vacancies according to the intensity $I_1 = 0.8$ derived from the positron lifetime measurements.

It turns out that the Doppler broadening data measured on MoSi$_2$ at 1343 K can be modeled at high electron momenta much better by the theoretical data obtained for vacancies $V_{Si}$ on the Si sublattice (see Fig. 5) than by the theoretical data for $V_{Mo}$. This demonstrates that thermal vacancies at high temperatures in MoSi$_2$ are preferentially formed on the Si sublattice, whereas vacancies $V_{Mo}$ on the Mo sublattice are negligible within the experimental uncertainty limits. If any contribution of $V_{Mo}$ would be taken into account by a combination of the theoretical curves in Fig. 5 this would lower the theoretical values and thereby deteriorate the fit to the experimental data.

A preferential formation of vacancies on the Si sublattice in MoSi$_2$ is also anticipated from the purely experimental data in Fig. 6. The high-temperature data for MoSi$_2$ exhibit the nonzero high-momentum slope typical for Mo atoms (curve $b$ in Fig. 6) which are available as nearest neighbors only for vacancies on the Si sublattice [see Fig. 1(b)].

The present studies of high-temperature vacancy formation can be directly employed for an immediate understanding of recent self-diffusion studies of $^{31}$Si [26] and of $^{95}$Mo [27] in MoSi$_2$. The diffusion of Si in MoSi$_2$ is demonstrated to be faster than that of Mo by more than 6 orders of magnitude, and an activation enthalpy $Q^{DD} = (2.3 \pm 0.1)$ eV is determined. From a simple approach for the diffusion activation enthalpy,

\[
Q = H^F_V + H^M_V \text{, a rather low value for the vacancy migration enthalpy of } H^M_V = 0.7 \text{ eV for MoSi}_2 \text{ can be anticipated taking into account the above value of } H^F_V = 1.6 \text{ eV. This indicates a high mobility of thermal vacancies on the Si sublattice of MoSi}_2.
\]

The high atomic diffusivity on the majority Si sublattice of MoSi$_2$ [26] can therefore be explained by a high vacancy concentration on the majority sublattice in combination with a high vacancy mobility or a low vacancy migration enthalpy.

A low value of the vacancy migration enthalpy $H^M_V$ in MoSi$_2$ is confirmed by considering the temperature dependence of the equilibration time of the thermal vacancy concentration [7]. This has been estimated from the shift of the first moments of the positron lifetime spectra after fast cooling from 1380 to 1073 or to 873 K. The mean positron lifetime characteristic for the lower temperatures was reached within less than 10 min, yielding an estimate of $H^M_V < 1.1$ eV by assuming a temperature
dependence of the time constant $t_E$ for thermal vacancy equilibration of $t_E^{-1} = t_{E,0}^{-1} \exp[-H^{0}_V/(k_BT)]$ and taking a value for $t_{E,0}^{-1} = 4 \times 10^3$ s$^{-1}$ similar to the values for other intermetallic compounds as B2-FeAl [10].

In conclusion, the present studies on the ordered intermetallic compound MoSi$_2$ demonstrate that, in addition to the detection of thermally formed vacancies by positron lifetime spectroscopy, the sublattice can be experimentally identified on which these vacancies are formed. This is of importance for understanding high-temperature solid state processes on an atomic level and of wide interest for understanding, e.g., diffusion mechanisms, order-disorder processes, solid state reactions, etc.

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