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 $H_V^F = (1.6 \pm 0.1)$ 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 binary ordered intermetallic compound MoSi$_2$ [see Fig. 1(a)] is a potential material for high-temperature structural applications [1]. The high-temperature properties [2–4] of intermetallic compounds are mainly determined by thermal defects such as vacancies. A study of the thermodynamic properties of thermally formed vacancies in MoSi$_2$ and particularly of the determination of the sublattice of the compound on which these thermal vacancies are formed is of particular interest for the understanding of these properties. The formation of thermal vacancies has been predicted on the transition-metal sublattice in some intermetallic compounds [5,6]. Recent positron lifetime and dilatometry experiments [7–10] have contributed to the understanding of thermal vacancy formation and migration in intermetallic compounds. These techniques are, however, incapable of determining the sublattice of an intermetallic compound on which the thermal vacancies are formed so that more specific techniques are desirable. Coincident measurements of the Doppler broadening of the positron-electron annihilation photons have been successfully employed in order to identify the location of radiation-induced vacancies [11,12]. By this technique the atomic chemical environment of the annihilation site, e.g., a vacancy has been analyzed by considering the high-momentum part of the electron momentum distribution [13–16]. In the present Letter we demonstrate that Doppler broadening measurements can be successfully employed in the exemplary case of MoSi$_2$ in order to identify the sublattices on which high-temperature vacancies are formed. This method might also be of general and wide interest for the studies of thermal atomic defects in complex solids.

For the present high-temperature positron annihilation studies, a positron source of ^{58}CoCl with an activity of 1.2×10^6 Bq was deposited inside the borehole of a cylinder prepared from a MoSi$_2$ single crystal [17], annealed in a hydrogen atmosphere, closed by a MoSi$_2$ cover, and sealed in a quartz tube under a pressure of $p < 10^{-3}$ Pa.

The positron annihilation lifetime spectra (time resolution 260 ps, 10^6 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 $E \geq (511 + 5)$ keV corresponding to $p_L \geq (19.6 \times 10^{-3})m_0c$ 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
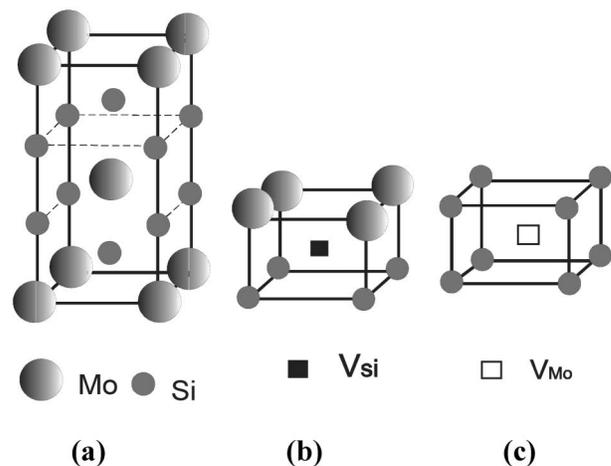
FIG. 1. Perfect and defected lattice structures of MoSi$_2$: (a) defect-free MoSi$_2$; (b) a vacancy located on the Si sublattice; (c) a vacancy located on the Mo sublattice.

the core-electron fractional contribution to the Doppler broadening spectra in the range of $\pm(20–28) \times 10^{-3} m_0 c$.

Theoretical studies of the positron annihilation Doppler broadening parameters were performed by using the wave functions of free atoms [19,20]. The total electron momentum distribution was obtained by summing up the contributions from each core-electron state weighted with its partial annihilation rate calculated by employing the generalized gradient approximation (GGA) of the electron-positron correlation [21].

The positron lifetime of $\tau = (117 \pm 1)$ ps determined 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 τ and the valence electron density of $MoSi_2$, $\rho_{el} = 338$ 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) $\tau_f(T) = \tau_{f_0}(1 + \alpha T)$ with $\tau_{f_0} = 117$ ps, the free positron lifetime at room temperature, and a thermal expansion coefficient $\alpha = 5 \times 10^{-5}$ K^{-1}, which is similar to the volume expansion coefficient of $\beta = 2.58 \times 10^{-5}$ K^{-1} [22]. A reversible S-shaped increase of the mean positron lifetime $\bar{\tau}$ is observed for $T > 1050$ K. This is attributed to positron trapping at thermally formed vacancies. The analysis of the positron lifetime spectra can be described by one type of thermal vacancy with a positron lifetime $\tau_1 = (165 \pm 5)$ ps.

For the two-state positron trapping model (see Ref. [7]), the positron trapping rate σC_V of thermally formed vacancies is given by

$$\sigma C_V(T) = \frac{\bar{\tau} - \tau_f}{\tau_f(\tau_1 - \bar{\tau})} = I_1\left(\frac{1}{\tau_0} - \frac{1}{\tau_1}\right), \quad (1)$$

with the vacancy concentration

$$C_V(T) = \exp\left(\frac{S_V^F}{k_B}\right)\exp\left(-\frac{H_V^F}{k_B T}\right). \quad (2)$$

Here, σ is the temperature-independent specific positron trapping rate, τ_f is the positron lifetime in the defect-free crystal, $\bar{\tau}$ 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 $\tau_0 = [(1/\tau_f) + \sigma C_V]^{-1}$ and τ_1 (characteristic for vacancies) as well as the relative intensities I_1 and $I_0 = 1 - I_1$ can be deduced from the analyses of the positron lifetime spectra.

A fit of the temperature variation of the mean positron lifetime

$$\bar{\tau}(T) = \tau_f \frac{1 + \sigma \exp(S_V^F/k_B) \exp(-H_V^F/k_B T)\tau_1}{1 + \sigma \exp(S_V^F/k_B) \exp(-H_V^F/k_B T)\tau_f}, \quad (3)$$

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

$$W(T) = W_f \frac{1 + \sigma C_V W_1}{1 + \sigma C_V W_f}, \quad (4)$$

where W_f and W_1 denote the W parameters characteristic for the defect-free compound and for saturation trapping

FIG. 2. Thermal formation of vacancies is indicated by the reversible S-shaped temperature variation of the mean positron lifetime $\bar{\tau}$. The solid line is a fit of Eq. (3) to the experimental data.
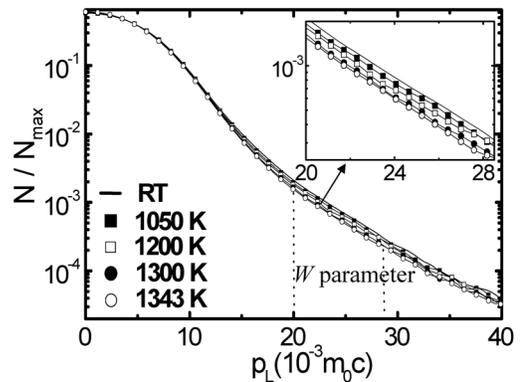
FIG. 3. Coincident Doppler broadening spectra measured for $MoSi_2$ at high temperatures. The spectra are normalized to the total number of counts. The high momentum range representing positron annihilation with core electrons as indicated is characterized by the W parameter.
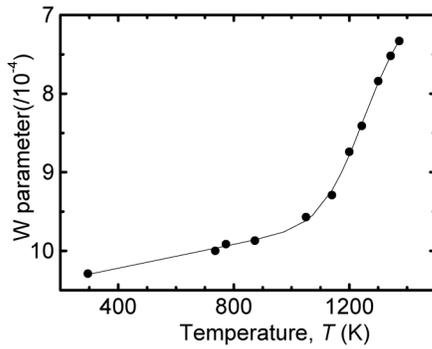
FIG. 4. Temperature variation of the W parameter in MoSi$_2$. The solid line is a fit to the data according to Eq. (4) (note the reversed ordinate scale).

FIG. 5. Ratio curves of the high-momentum part of the electron momentum distribution for a MoSi$_2$ single crystal at 1343 K (■) and the calculated data for the vacancies V_{Si} and V_{Mo} on the two sublattices of MoSi$_2$. The experimental and theoretical data for vacancy trapping were normalized to the experimental and theoretical data of defect-free bulk MoSi$_2$ (see the inset) at ambient temperature. No atomic relaxation around the vacancies is considered. The experimental data for MoSi$_2$ at 1343 K are scaled to full trapping at thermal vacancies by making use of the intensity $I_1 = 0.8$ derived from the positron lifetime measurements, which yields a fraction of trapped positrons $\eta = 0.54$. The theoretical results are not valid at low momenta (shaded area) due to the omission of the valence electron contribution in the calculations. The calculated ratio curve of the high-momentum part for vacancies on the Si sublattice (V_{Si}) is in good agreement with experimental data of the MoSi$_2$ at 1343 K, demonstrating that thermal vacancies are formed preferentially on the Si sublattice of the MoSi$_2$.

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 $H_V^F = (1.7 \pm 0.1)$ 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 $H_V^F/k_B T_M = 8.0$ similar to the low values $H_V^F/k_B T_M = 7.0$ 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 ^{99}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 $Q^{SD} = (2.3 \pm 0.1)$ eV is determined. From a simple approach for the diffusion activation enthalpy, $Q = H_V^F + H_V^M$, a rather low value for the vacancy migration enthalpy of $H_V^M = 0.7$ eV for MoSi$_2$ can be anticipated taking into account the above value of $H_V^F = 1.6$ 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_V^M 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 $H_V^M < 1.1$ eV by assuming a temperature
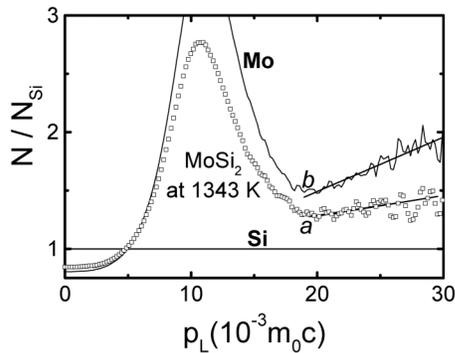
FIG. 6. Ratio curves of the coincidently measured Doppler broadening spectra of pure Mo and of pure Si at ambient temperature as well as that of MoSi$_2$ at 1343 K. All spectra are normalized to the spectrum of defect-free pure Si. The slopes a for MoSi$_2$ at 1343 K and b for the pure Mo are determined by fitting the data in the range of $[(20-28) \times 10^{-3}]m_0c$. The value for slope a lies between slope b of pure Mo and the horizontal line of pure Si indicating a Mo contribution as well as a Si contribution. Thus, the vacancy environment contains Mo atoms indicating the formation of thermal vacancies on the Si sublattice (see V_{Si} in Fig. 1).

dependence of the time constant t_E for thermal vacancy equilibration of $t_E^{-1} = t_{E,0}^{-1} \exp[-H_V^M/(k_B T)]$ and taking a value for $t_{E,0}^{-1} = 4 \times 10^5$ 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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