Defect evolution during the phase transition of hexagonal nickel sulfide studied by positron annihilation spectroscopy

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\section{A R T I C L E   I N F O}

Article history:
Received 14 March 2014
Received in revised form 24 October 2014
Accepted 3 November 2014
Communicated by “P. Hawrylak”

Keywords:
Phase transition
Ni-monovacancy
Positron annihilation spectroscopy

\section{A B S T R A C T}

The defect structures of the hexagonal nickel sulfide with different Ni contents (Ni\textsubscript{1-x}S) have been investigated mainly by the positron annihilation lifetime spectroscopy and the temperature-dependent positron Doppler broadening technique. Combining with theoretical calculations, it is convincingly found that there is a high concentration of Ni-monovacancies in Ni\textsubscript{1-x}S not only in the low temperature (LT) phase but also in the high temperature (HT) phase. The defect concentration and the trapping functionality for positrons have almost no changes before and after the phase transition. Besides, the transition temperature decreases and the thermal hysteresis width of the phase transition narrows down with the reduction of Ni contents, since the existence of Ni-monovacancies can lower the energy requirement of the transformation and thus promote the transition occurrence.

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\section{1. Introduction}

Nickel sulfide (NiS) has two well-characterized polymorphs, a rhombohedral phase (β-NiS) under ambient condition and a hexagonal phase (α-NiS) at temperature above 620 K which can be maintained by quenching to room temperature [1,2]. Especially, the hexagonal NiS has received considerable attention nearly half a century due to its interesting electronic and structural phase transitions [3–6]. It exhibits a first-order phase transition when the temperature or pressure is increased. At a temperature greater than the transition temperature \(T_t \sim 265\) K, it has the highly conducting Pauli paramagnetic metallic state (the HT phase), while for \(T < 265\) K, it has the antiferromagnetic nonmetallic state with nearly temperature independent resistivity [7], and the lattice parameters \(a, c\) and the volume of the unit cell in the hexagonal NiS show an increase [1]. The Hall effect experiments on Ni\textsubscript{1-x}S with different values of \(x\) have indicated that the majority carriers in the LT phase are holes with a density proportional to Ni vacancies [8]. Besides, the transition temperature is lowered sharply with increasing Ni vacancy concentration and the transformation disappears when the vacancy contents exceed \(\sim 4\%\). Similar behavior is also observed with applied pressure: the transition doesn’t happen at pressure above \(\sim 2\) GPa [9]. Those related experimental results could be found in Refs. [8,10]. Many other basic physical properties of the hexagonal NiS can be found in the related Refs. [11–13]. As Hall coefficients could not be observed in the HT phase [8], the defects in that phase are inconclusive. Moreover, the changes of the type and concentration of the defects during the phase transition in hexagonal NiS have not been discussed.

Positron annihilation techniques [14] are considered as a unique probe with a sensitivity of \(10^{-6}\) ppm order, with which the vacancy-type defects can be directly detected. The positron lifetime experiment at room temperature performed by Noguchi et al. [15] concluded that the Ni vacancies could not trap the positrons in the HT phase of hexagonal NiS but would have an opposite behavior in the LT phase. In this paper, through positron-related experiments and theoretical calculations, it is found that there is a high concentration of Ni-monovacancies in Ni\textsubscript{1-x}S, and the concentration of this kind of defect has almost no changes before and after the phase transition. This provides direct evidence that Ni vacancies could trap the positrons not only in the LT phase but also in the HT condition, which is different with the reported Ref. [15]. In addition, we attempt to explain the phenomena that the transition temperature decreases and thermal hysteresis width of the phase transition narrows with the deficient Ni contents.

\section{2. Experimental section}

The polycrystalline samples of α-Ni\textsubscript{1-x}S (\(x \approx 0.02, 0.03\) and 0.05) were prepared following the standard solid-state reaction techniques reported in Refs. [9,16]. X-ray diffraction patterns were
performed by the MAX 18 AHF X-ray diffractometer with Cu Kα radiation (\(\lambda=1.54056\) Å). The temperature dependence of electrical resistance of the samples was measured by the standard four-probe method. Before taking the positron experiments, the tested samples in powder forms were pressed into sheets with an external pressure of about 18 MPa. The positron lifetime (PL) experiment was performed with a fast-slow coincidence ORTEC system with a time resolution of about 230 ps. A 5 \(\mu\)Ci radioactive source of \(^{22}\)Na was sandwiched between two identical samples and the total count for each lifetime spectrum was two million. The temperature-dependent coincidence Doppler broadening spectra (CDB) was measured using two HP-Ge detectors with a counting rate of approximately 100 cps (the source intensity is 30 \(\mu\)Ci). The energy resolutions of the two detectors were about 1.5 keV at the energy of 0.511 MeV which corresponds to the positron 2\(\gamma\) annihilation peak. The total count for each CDB spectrum at different temperature was 5 million. For more details about the positron-related experimental techniques, please see Ref. [15].

3. Positron lifetime calculation

The so-called atomic superposition (ATSUP) method which was first established by Puska and Nieminen was carried out here [17]. It is a simple but already very valuable model for constructing positron states in solids. In fact, it has been extensively used in the positron lifetime estimation and proved to be useful, especially in complex systems [18]. In ATSUP, the electron density is constructed by superimposing densities of neutral free atoms (Equation 55 in Ref. [15]); the positron’s potential is a sum of Coulomb potentials due to the superimposed free atoms and a positron-electron correlation potential (Equation 56 in Ref. [15]). So far, about three models have been introduced to deal with the positron-electron correlation potential and the enhancement factor. They are weighted-density approximation (WDA), local density approximation (LDA) and general gradient approximation (GGA). However, the WDA has not been applied for positrons trapped at vacancies. In other words, it has not yet carried out the effective test to handle the defect systems. Therefore, both LDA and GGA schemes were adopted in this paper. Since the positron lifetime experiment was performed at room temperature, samples M2 and M3 were in metallic states. The high frequency dielectric constants needed in positron 2\(\gamma\) annihilation peak. The total count for each CDB spectrum at different temperature was 5 million. For more details about the positron-related experimental techniques, please see Ref. [15].

4. Results and discussion

X-ray diffraction patterns are shown in Fig. 1. These results agree well with the reported data in Refs. [19,20]. The material-1 (we call it M1 briefly) is mainly the \(\beta\)-NiS. Material-2 (M2) with \(\Delta \approx 0.03\) and material-3 (M3) with \(\Delta \approx 0.02\) have the \(\alpha\)-NiS structure. The calculated lattice parameters of \(\alpha\)-NiS are \(a=3.434\) Å and \(c=5.377\) Å. In this paper, we focus on the defects study of M2 and M3.

The PL results of M2 and M3 are shown in Fig. 2a, and the third lifetime component which mainly reflects the \(\alpha\)-Ps annihilation are very small (smaller than 1%) in both samples. Therefore, the spectra displayed in Fig. 2a are all made up of two lifetime components. In Table 1, there is a relatively high concentration of the first lifetime component but much low for the second. The intensity of the first lifetime in M2 is a little stronger than in M3.

Based on the ATSUP method, the positron lifetimes for many kinds of defects have been estimated. Before showing the results, it should be noted that there are many kinds of configurations of Ni-divacancy. However, they could be divided into two categories roughly as shown in Figs. 3a and 4a. One of them is the adjacent configuration which could be referred to as AC briefly. Fig. 3a is just an example, and other adjacent configurations are not displayed. The other is the non-adjacent case which could be called simply NAC as shown in Fig. 4a, and similar to AC situation, other non-adjacent configurations are not exhibited. The theoretical positron lifetimes within LDA and GGA schemes are provided in Table 2. In this table, \(V_{3S}\), \(V_{2S}\) and \(V_{S}\) represent the S-monovacancy, S-divacancy and Ni-monovacancy, respectively. Figs. 3b and 4b provide the isosurfaces of the positron density for a...
Table 1
Experimental positron lifetime components of M2 and M3.

<table>
<thead>
<tr>
<th>Material</th>
<th>r1 (ps)</th>
<th>h1 (%)</th>
<th>r2 (ps)</th>
<th>h2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2</td>
<td>193</td>
<td>96.8</td>
<td>361</td>
<td>3.2</td>
</tr>
<tr>
<td>M3</td>
<td>188</td>
<td>94.3</td>
<td>352</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Fig. 3. (a) One of the adjacent configurations (AC) of Ni-divacancy; (b) isosurface of the positron density for a positron localized at the AC Ni-divacancy.

Table 2
Theoretical positron lifetimes of different defect configurations: S-monovacancy (V_s), S-divacancy (V_{2s}), Ni-monovacancy (V_{Ni}), adjacent configurations and non-adjacent configurations of Ni-divacancy (V_{2Ni} (AC) and V_{2Ni} (NAC)).

<table>
<thead>
<tr>
<th>Defect configuration</th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>137</td>
<td>159</td>
</tr>
<tr>
<td>V_s</td>
<td>195</td>
<td>202</td>
</tr>
<tr>
<td>V_{2s}</td>
<td>216</td>
<td>224</td>
</tr>
<tr>
<td>V_{Ni}</td>
<td>164</td>
<td>178</td>
</tr>
<tr>
<td>V_{2Ni} (AC)</td>
<td>201</td>
<td>212</td>
</tr>
<tr>
<td>V_{2Ni} (NAC)</td>
<td>171</td>
<td>183</td>
</tr>
</tbody>
</table>

Fig. 4. (a) One of the non-adjacent configurations (NAC) of Ni-divacancy; (b) isosurface of the positron density for a positron localized at the NAC Ni-divacancy.

The LDA results are usually smaller than GGA for that the LDA systematically overestimates the annihilation rates of positrons in solids, which have been proved from many positron experiments [21]. Indeed, generally speaking LDA overestimates the annihilation contributions from core electrons, but underestimates the proportions for valence electrons. That could also happen in hexagonal NiS system as displayed in Fig. 5. Fig. 5a is the contour map of positron distribution obtained from GGA in an atomic plane of defect-free structure. Because of the nuclear repulsion, the positrons are mainly in interstitial area between host atoms.

So far, the GGA has been considered as the most accurate approach to predicting the absolute values of positron lifetime in solid materials [18,14]. This is also true in NiS, and hence we should focus on the GGA results while analyzing the positron lifetime experiments. In addition, from the first-principle pseudopotential estimation, it is found that the defect formation energies of S-monovacancy and S-interstitial are much larger than Ni-monovacancy even in the Ni-rich and S-rich conditions. Indeed, in Ni-rich condition, \( E[V_s] - E[V_{Ni}] \approx 2.65 \text{ eV} \), and in S-rich condition, \( E[S\text{-interstitial}] - E[V_{Ni}] \approx 3.42 \text{ eV} \), where \( E[V_s], E[V_{Ni}] \) and \( E[S\text{-interstitial}] \) represent the defect formation energies of S, Ni, and S-interstitial, respectively. It means high concentrations of S vacancy or interstitial could not appear in the samples. Therefore, the phase transition has little even nothing to do with the S-defects, and the samples should be labeled as Ni_{1+x}S but not NiS_{1+x}.

Because the atom S has a little larger particle size than atom Ni, the calculated positron annihilation lifetimes are greater in S-vacancies than in Ni-vacancies. Many non-adjacent configurations of Ni-divacancies have been taken into consideration, and all of them produce almost the same positron lifetime which is \( \approx 183 \text{ ps} \) within GGA. By comparing Table 1 with Table 2, it is concluded that the first lifetime component \( \tau_1 \) comes from the positrons from the annihilation in Ni-monovacancies or in Ni-divacancies which are in the NAC situation. In addition, if two Ni-monovacancies which constitute a Ni-divacancy are far away from each other, the interaction between them could be ignored. Under this circumstance, a NAC Ni-divacancy could be considered as two monovacancies. Besides, from the first-principle calculation, the Ni-divacancy shown in Fig. 4a has larger defect formation energy than Ni-monovacancy and the specific value \( E[Ni\text{-divacancy}] - E[Ni\text{-monovacancy}] \approx 3.07 \text{ eV} \). Therefore, it can be deduced that the \( \tau_1 \) with a high concentration in Table 1 reflects the positrons annihilation in Ni-monovacancies, and this directly demonstrates that the Ni-monovacancies could trap the positrons. The second lifetime component \( \tau_2 \) with a smaller proportion mainly reflects the positrons pick-off annihilation at the boundary of the polycrystalline sample. In addition, \( \tau_2 \) and \( \tau_3 \) for both samples have almost the same values, implying that the electron distributions at the boundaries for the two materials are similar with each other.

In order to study the trapping nature for further, the temperature-dependent CBD experiments have been carried out and the S-parameters at different temperatures are shown in Fig. 2b. There are no significant changes in S-parameters within the testing temperature range (60–230 K) for the two samples, and the mean value of the S-parameter in M2 is a little larger than in M3. It can be concluded that the S-parameters mainly reflect the positron annihilation in Ni-monovacancies but not at the boundaries in the HT phase (corresponding to the first lifetime components in Table 1, there is a little stronger intensity in sample M2 than in M3). Moreover, the defects of the LT phase confirmed by the Hall effect experiment are also Ni vacancies [8,9]. Therefore, it can be seen that the Ni-monovacancy concentration remains nearly constant in the process of phase transition from the temperature-dependent CBD experiments. It provides a direct support for our suggestion that the Ni-monovacancies could trap positrons not only in the LT phase but also in the HT condition. The trapping ability of Ni-monovacancies to positrons has almost no changes before and after the phase transition. Besides, the Ni-monovacancy concentration in M2 is a little larger than in M3, which directly demonstrates that the concentration of Ni-monovacancies in a sample increases with the decreasing Ni contents. Fig. 6a shows the temperature dependence of the electrical resistance of samples. The heating and cooling processes are labeled in the picture. It is easy to see that \( \beta \)-NiS (M1) exhibits
metallic behavior in the whole range of testing temperature, and the resistance is about $10^{-3} \, \Omega$. In contrast, when temperature $T$ decreases ($< \sim 210 \, K$), the resistances of M2 and M3 increase (changing from $\sim 10^{-3} \, \Omega$ to $\sim 0.1 \, \Omega$ in M3). However, when $T > \sim 210 \, K$, both of the samples behave as metal as shown in the insert map in Fig. 6a. Fig. 6b is the differential curves, and the determined transition temperature of M2 and M3 are about 138.5 K and 150.5 K, respectively. Combining with the results of positron-related experiments and theories, it could be found that the resistance of the LT phase drops with the increasing Ni-monovacancy concentration. The reason is that creating one Ni-monovacancy will introduce two hole carries, and the carrier monovacancy concentration. The reason is that creating one Ni-monovacancy will introduce two hole carries, and the carrier monovacancy concentration. 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