is too small to account for the discrepancy. Their metal "2p" levels are likewise displaced by about the same amount from the values reported here. It is probable that these differences reflect a significant calibration error in the results of Domhshevskaya and co-workers[17] since the data reported in the present study are in reasonably good agreement with data obtained by others[32,33] for the elements and for similar compounds. The $2p_{3/2}$ binding energies of metal and phosphorus show a maximum shift from the positions for the respective elements in the case of ScP, with a regular decrease in the shifts as the number of metal d electrons increases. The shifts in phosphorus peaks are greater and decrease more gradually than do the shifts in the metal peaks, presumably because of better shielding of the metal atoms by the conduction electrons. The trends are interpreted as evidence for decreasing ionicity, which is consistent with trends in the conduction band spectra and with the changes in crystal structure through the series of monophosphides. These observations are also consistent with shifts observed in related sulfides,[34] which were interpreted to mean that the occurrence of metallic interactions to form a d band diminishes the tendency toward ionicity in the metal–nonmetal interactions, and this results, for the sulfides, in almost neutral (i.e., with negligibly shifted core levels) atomic species in the solid.

In addition to these trends within the phosphide series, there are important differences between the phosphides and the corresponding sulfides. Whereas ScP, a nominally saturated valence compound, is somewhat ionic, ScS is metallic with no net scandium to sulfur electron transfer.[22] On the other hand, MnS is rather ionic,[34] but there is little net electron transfer in MnP. In the former example, both ScP and ScS have the NaCl-type structure,[14] but in ScS there are more than enough electrons to fill the valence band, and there is significant electron delocalization. MnS has the NaCl-type structure, and its ionic nature is attributable to the electrons in the half-filled d shell not being available to form a conduction band. In contrast, MnP has one less electron per nonmetal atom, and its structure is a distortion of the NiAs-type structure, which affords significant metal–metal bonding.

Acknowledgment. The authors wish to thank Elizabeth L. Patterson for preparation of some of the samples used in this study and for assistance in making the measurements and Thuy-Hoa Nguyen for helpful discussions. This research was supported by the Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contracts W-7405-Eng-82 at Iowa State University and DEAC02-78ER04948 at the State University of New York at Binghamton. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under the above contract. Partial travel support was provided by the Research Foundation of the State University of New York.

Registry No. ScP, 12202-43-6; TiP, 12037-65-9; VP, 12066-53-4; MnP, 12032-78-9; FeP, 26508-33-8.

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Effects of Sodium Intercalation in TiS_2 on the Electronic Structure of a TiS_2 Slab

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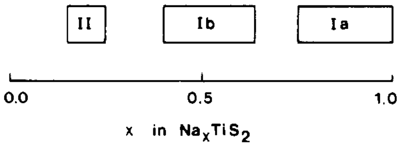
Received October 26, 1984

The band electronic structure of a TiS_2 slab was calculated as a function of the slab thickness by employing the tight-binding method. Flattening of a TiS_2 slab beyond a certain critical value is found to increase not only the density of states at the Fermi level for Na_xTiS_2 but also the anisotropy of electron distribution around Ti^{4+}. This explains why there occurs an abrupt increase in both the isotropic and anisotropic parts of the ^{23}Na Knight shifts in Na_xTiS_2 upon the Ib → Ia phase transition.

Alkali-metal intercalation in layered transition-metal dichalcogenides has been the subject of numerous studies.[1] Sodium intercalation in TiS_2 has been found to give several distinct Na_xTiS_2 phases.[2] Accurate boundaries of these phases are difficult to ascertain, but all studies[2] reveal the presence of three single phases in the concentration range $0.15 < x \leq 1$. The phase boundaries determined recently by Molinie et al.[2h] from X-ray measuremens are shown in **1**, where the II, Ib, and Ia phases span the concentration ranges $0.15 < x < 0.25$, $0.40 < x < 0.64$, and $0.75 < x \leq 1$, respectively. Phase II is a second-stage compound while the other two are first-stage compounds.



Structures of Na_xTiS_2 are often characterized by the crystal *a* and *c* parameters, where the *c* axis is perpendicular to a TiS_2 slab. As shown in **2** each Ti^{4+} ion is octahedrally coordinated, where the *a* parameter (i.e., the repeat distance within a TiS_2 slab) coincides with the length of a side of S_3^{6-} triangle. In **2** and **3** the thickness of a TiS_2 slab is denoted by d_t, and the interlayer separation between adjacent TiS_2 slabs by d_s. Thus the *c* parameter (i.e., the repeat distance along the *c* axis) is given by *d*

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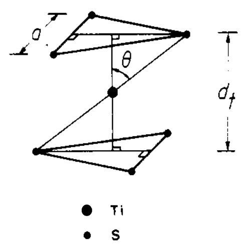

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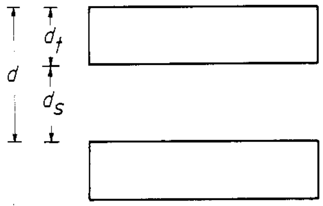

(=d_t + d_s) in TiS_2 but by 3d in the Ib and Ia phases of Na_xTiS_2. That is, a unit cell of phase Ib or Ia has three TiS_2 slabs, arising from the manner in which sodium intercalates between TiS_2 slabs. Concerning the coordination environment of sodium ions, phases Ib and Ia are quite different in that sodium ions are located at trigonal-prismatic sites in phase Ib but at octahedral sites in phase Ia.[1,2]

The first two columns of Table I list the a and c values of TiS_2 and those of representative phase Ib and phase Ia Na_xTiS_2 compounds (e.g., $x = 0.5$ and 0.9 for phases Ib and Ia, respectively).[2h] Compared with TiS_2, phase Ib has a slightly larger a value but a significantly larger d value, the latter being a direct consequence of sodium intercalation. With respect to phase Ib, phase Ia has a substantially greater a value but a substantially smaller d value. Within phase Ib or Ia, the a and d values vary smoothly as a function of x.[2h] On passing the phase boundary from Ib to Ia, however, the a value increases abruptly while the d value decreases abruptly. To characterize the Ib → Ia phase transition Molinie et al.[2h] carried out an extensive NMR study by measuring ^{23}Na Knight shifts.[3] Given the isotropic and anisotropic parts of the Knight shift as K_{iso} and K_{ax}, respectively, the essence of their results may be summarized as follows: (a) At the Ib → Ia phase transition there is a jump of K_{iso}, which is nearly twice as large in phase Ia as in phase Ib. (b) K_{ax} is negligible in phase Ib, but this is not the case in phase Ia. Qualitatively, the magnitude of Knight shift increases with the density of states at the Fermi level, $n(e_f)$,[3] so that result a indicates $n(e_f)$ to increase abruptly upon the Ib → Ia phase transition.[2h] However, this change in $n(e_f)$ alone cannot explain result b unless the increase in $n(e_f)$ involves some anisotropic charge distribution around the sodium ions.

The Knight shift results of Molinie et al. suggest that the Ib → Ia phase transition takes place with a change in the band electronic structure of Na_xTiS_2.[2h] This is difficult to understand unless TiS_2 slabs are modified in some way during the phase transition. Within each TiS_2 slab strong ionocovalent bonding exists between Ti and S. Thus it is reasonable to assume that the Ti–S bond distance remains constant during the course of sodium intercalation. This permits us to calculate the structural parameters θ, d_t, and d_s (see **2** and **3**) of Na_xTiS_2 listed in the last three columns of Table I, which shows that the Ib → Ia phase transition not only flattens each TiS_2 slab but also shortens the interlayer separation. In understanding the seemingly puzzling behavior of the ^{23}Na Knight shift data, it is therefore imperative to examine how the electronic structure of a TiS_2 slab is affected by a change in the slab thickness d_t (equivalently, by that of the angle θ or the a value). This question was probed in the present work by performing tight-binding band calculations[4] on a TiS_2 slab as a function of the angle θ. The atomic parameters employed in our calculations are summarized in Table II.

Table I. Structural Parameters for Na_xTiS_2[a]

compd	a	c	d_t	d_s	θ
TiS_2	3.406	5.697 × 1	2.845	2.852	54.1
$Na_{0.5}TiS_2$[b]	3.440	7.010 × 3	2.790	4.220	54.9
$Na_{0.9}TiS_2$[c]	3.550	6.660 × 3	2.600	4.060	57.6

[a] a, c, d_t, and d_s values are in angstroms; θ values are in degrees. [b] A representative of phase Ib. [c] A representative of phase Ia.

Table II. Exponents ζ_μ and Valence-Shell Ionization Potentials $H_{\mu\mu}$ for Slater Type Orbitals X_μ[a,b]

X_μ	ζ_μ	ζ_μ'	$H_{\mu\mu}$, eV
Ti 4s	1.075		−8.9
Ti 4p	0.675		−6.5
Ti 3d	4.55 (0.4206)	1.40 (0.7839)[c]	−11.1
S 3s	1.817		−20.0
S 3p	1.817		−13.3

[a] The d orbitals of Ti are given as a linear combination of two Slater type orbitals, and each is followed by weighting coefficient in parentheses. [b] A modified Wolfsberg–Helmholz formula was used to calculate $H_{\mu\nu}$.[11] [c] Reference 12.

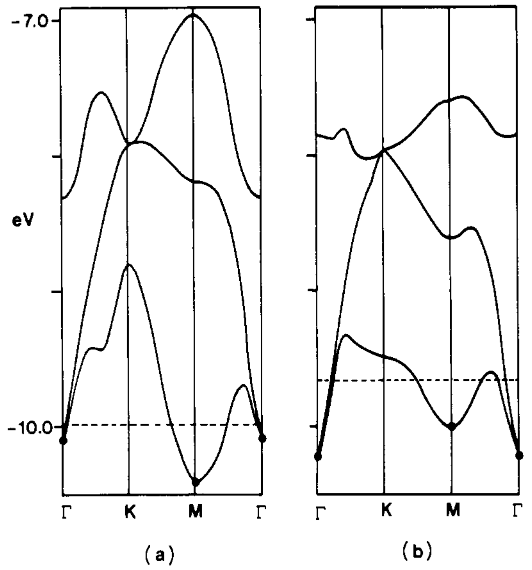

Figure 1. Calculated t_{2g} subbands of a TiS_2 slab: (a) θ = 54.9°; (b) θ = 57.6°. The dotted lines are the Fermi levels appropriate for (a) $Na_{0.5}TiS_2$ (a) and (b) $Na_{0.9}TiS_2$.

Results and Discussion

A. Band Structure. In the past a number of band electronic structure calculations have been carried out on TiS_2.[5] The formal oxidation state of $Ti^{4+}(S^{2-})_2$ suggests that the d-block bands of TiS_2, lying above the s,p-block bands primarily sulfur in character, are not occupied. Since each Ti^{4+} ion is octahedrally coordinated, the d-block bands are expected to consist of three bands derived largely from the t_{2g} level of Ti^{4+} (hereafter referred to as the t_{2g} subbands), which lie below two bands derived largely from the e_g level of Ti^{4+}. All of these expectations are borne out by the results of various band structure studies including the present one.

Since sodium atoms are present as Na^+ cations in Na_xTiS_2,[1,2] it is the t_{2g} subbands that become partially filled upon sodium intercalation. Figure 1a shows the t_{2g} subbands of a phase Ib, calculated for a TiS_2 slab of θ = 54.9° as found in $Na_{0.5}TiS_2$.

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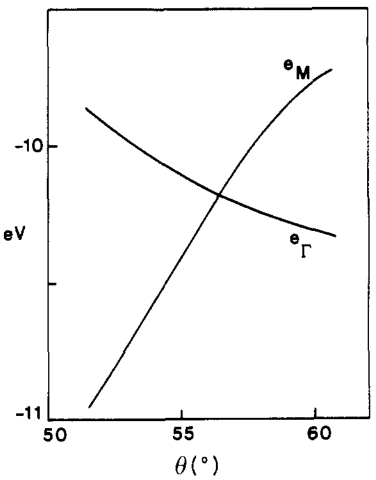

Figure 2. Variation of the e_Γ and e_M levels as a function of θ.

Likewise, Figure 1b shows the t_{2g} subbands of a phase Ia, calculated for a TiS_2 slab of $\theta = 57.6°$ as found in $Na_{0.9}TiS_2$. The dotted lines of Figure 1 refer to the Fermi levels appropriate for Na_xTiS_2, which were determined by simply filling the t_{2g} subbands with x electrons per unit cell. Not surprisingly, the gross features of parts a and b of Figure 1 are similar. Nevertheless, we observe two important differences between the two at the bottom portion of the t_{2g} subbands: (a) The lowest lying band is narrower in bandwidth in phase Ia than in phase Ib. (b) In phase Ib the lowest energy point at $\mathbf{\Gamma}(e_\Gamma)$,[6] which is doubly degenerate, lies higher in energy than the lowest energy point at $\mathbf{M}(e_M)$, as is also found by other calculations with a TiS_2 slab of $\theta \simeq 54.1°$.[5a–c,7] In phase Ia, however e_Γ lies lower in energy than e_M. These two differences are critical since it is only the bottom portion of the t_{2g} subbands that become filled by sodium intercalation. It is noted that the t_{2g} subbands as a whole would be one-sixth filled at most, which occurs for $NaTiS_2$.

The e_Γ and e_M levels vary smoothly as a function of θ, as shown in Figure 2. e_Γ becomes lower in energy than e_M beyond $\theta = 56.4°$, at which the a value is calculated to be 3.50 Å. These θ and a values at the crossing point of Figure 2 may be denoted by θ_{cr} and a_{cr}, respectively. It was experimentally found[2h] that, on passing the phase boundary from Ib to Ia, the a value changes abruptly from ~3.45 to ~3.53 Å. The calculated a_{cr} value of 3.50 Å lies between those two values. Consequently, we expect that the change in the relative ordering of the e_Γ and e_M levels, which is a consequence of flattening a TiS_2 slab, might provide a key for understanding the ^{23}Na knight shift data of Molinie et al.[2h]

B. Density of States and Phase Transition. How the density of states of a TiS_2 slab depends on a change in the slab thickness was examined in the present study by calculating the density of states as a function of θ based upon the special **k**-point method.[8,9] Our results are summarized in Figure 3, which shows the density of states at the Fermi level $n(e_f)$ as a function of x for several different θ values. Curves a, b, c, and d refer to the slabs of θ = 54.9, 56.2, 57.6, and 59.1°, respectively. It is clear from Figure 3 that the change in $n(e_f)$ is quite abrupt as the θ value crosses the θ_{cr} point (56.4°) toward phase Ia and that the $n(e_f)$ value is much greater in phase Ia than in phase Ib. The latter observation is related to the fact that the lowest band of the t_{2g} subbands is much narrower in phase Ia than in phase Ib, as already noted from Figure 1. From curves a and c of Figure 3, the $n(e_f)$ value is calculated to increase by about 25% on going from $Na_{0.5}TiS_2$ to $Na_{0.9}TiS_2$. The corresponding increase in the K_{iso} value is observed to be about 65%.[2h] These findings are mutually consistent.

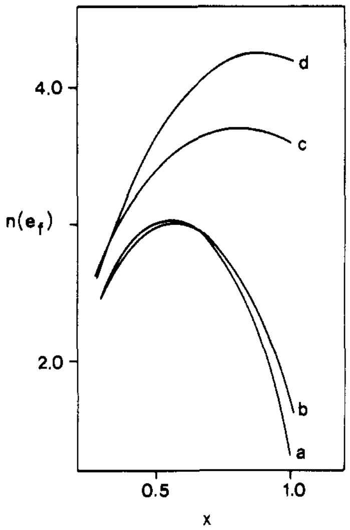

Figure 3. Variation of $n(e_f)$ as a function of x. $n(e_f)$ is in units of electrons per unit cell per electronvolt. Curves a, b, c, and d refer to θ = 54.9, 56.2, 57.6, and 59.1°, respectively.

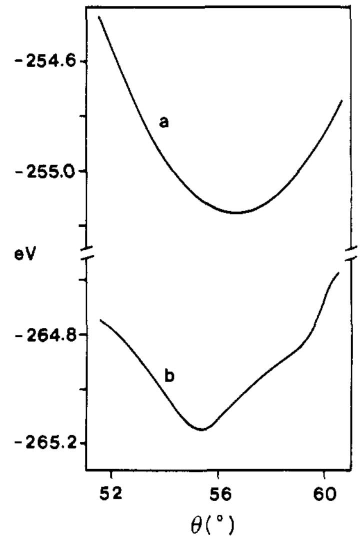

Figure 4. $\langle E \rangle$ vs. θ plots for Na_xTiS_2: (a) $x = 0$; (b) $x = 1$.

According to Figure 1, the occupied d-block electrons of phase Ib are represented primarily by the band orbitals around the wavevector **M** while those of phase Ia are represented primarily by the band orbitals around the wavevector **Γ**. With the coordinate z axis taken along the c axis of a TiS_2 slab, analyses of band orbital components show that the band orbitals representing e_Γ do not have contribution from z^2 orbitals and those around e_Γ have only a small contribution from z^2 orbitals. This is not the case for the band orbitals around e_M, in which all components of d orbitals are found. Thus the occupied d-block electrons are associated with much greater anisotropic electron distribution around Ti^{4+} in phase Ia than in phase Ib. This would create a stronger anisotropy in the electron distribution around Na^+ in phase Ia and hence give rise to greater K_{ax} values in phase Ia.

Finally we have calculated the total electronic energy of a TiS_2 slab per unit cell, $\langle E \rangle$, as a function of θ and x so as to examine the energetic factors responsible for the Ib → Ia phase transition. The $\langle E \rangle$ vs. θ plots for $x = 0$ and 1 are given by curves a and b of Figure 4, respectively. The θ value of 56.5° at the energy minimum of curve a is slightly greater than the experimental θ

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(6) The symbols **Γ**, **M**, and **K** are the special points (0, 0), ($^1/_2$, 0)a^*, and ($^1/_3$, $^1/_3$)a^*, respectively, of the first Brillouin zone appropriate for a TiS_2 slab. For details, see: Lax, M. "Symmetry Principles in Solid State and Molecular Physics"; Wiley: New York, 1974.

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(9) We employed the 6-**k** point set. The wavevectors $\mathbf{k}_i$ and their weighting factors w_i are given as follows: $\mathbf{k}_1 = (^1/_9, ^1/_9)a^*$, $w_i = ^1/_9$; $\mathbf{k}_2 = (^2/_9, ^2/_9)a^*$, $w_2 = ^1/_9$; $\mathbf{k}_3 = (^4/_9, ^4/_9)a^*$, $w_3 = ^1/_9$; $\mathbf{k}_4 = (^1/_3, ^1/_9)a^*$, $w_4 = ^2/_9$; $\mathbf{k}_5 = (^5/_9, ^1/_9)a^*$, $w_5 = ^2/_9$; $\mathbf{k}_6 = (^4/_9, ^2/_9)a^*$, $w_6 = ^2/_9$.

value of 54.1° found in TiS_2. Comparison of curves a and b shows that electron filling of the t_{2g} subbands decreases the θ value slightly, which is a reflection of the fact that the bottom portion of the t_{2g} subbands is low in energy for small θ (see Figures 1 and 2). Consequently, electron filling of the t_{2g} subbands itself cannot be responsible for the Ib → Ia phase transition, so that the cause for this transition must be associated with ionic interactions of Na^+ cations with sulfur layers of TiS_2 slabs. It is worth noting that no phase transition such as Ib → Ia is present in intercalation of TiS_2 with alkali metal atoms other than sodium.[1,2b,10]

Concluding Remarks

It is often assumed that intercalation of a layer compound does not modify slabs of the host. That this is not necessarily the case was strongly suggested by the work of Molinie et al.[2h] on Na_xTiS_2. The present study shows that the abrupt change in the ^{23}Na Knight shifts at the boundary of phases Ib and Ia is due primarily to the flattening of a TiS_2 slab beyond the critical a_{cr} value of 3.50 Å. (Note that the larger the a value, the more flattened is a TiS_2 slab.) This structural change brings about an abrupt increase not only in $n(e_f)$ but also in the anisotropy of electron distribution around Ti^{4+}. Can we expect such a drastic change in electronic structure for other alkali-metal intercalations in TiS_2? In the first-stage compound of various A_xTiS_2 (A = Li, K, Rb, Cs), the a value is found to increase gradually with x.[10] However, in none of those systems, does the maximum a value exceed the critical value $a_{cr} = 3.50$ Å. Therefore an abrupt change in band electronic structure such as the one observed for the Ib → Ia phase transition in Na_xTiS_2 is not expected for other alkali-metal intercalations in TiS_2.

In the present study we have considered only ideal stoichiometric TiS_2, but nonstoichiometric situations arise in the form of $Ti_{1+y}S_2$ (usually $y \simeq 0.005$). This nonstoichiometry would lead to slightly populated d-block bands in the absence of sodium intercalation, which might slightly change the phase boundaries of Na_xTiS_2 but not the conclusions of the present study.

Acknowledgment. This work was in part supported by the Camille and Henry Dreyfus Foundation through a Teacher-Scholar Award to M.-H.W.

Registry No. TiS_2, 12039-13-3; sodium titanium sulfide, 12624-30-5.

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Reaction of Triethylenetetramine with Nickel(II) *N,N'*-Diglycylethylenediamine

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The reaction of triethylenetetramine with nickel(II) *N,N'*-diglycylethylenediamine, $NiH_{-2}DGEN$, proceeds through trien$_t$-dependent and -independent pathways. The rate constants for the trien species cannot be resolved, but their ratios are $k_{HT}/k_T = 0.63$ and $k_{H_2T}/k_T = 0.046$. The rate constant for the dissociation of a terminal amine group from nickel(II) is 0.08 s^{-1}. The reaction is specific hydrogen ion dependent with a rate constant $k_{H_3O} = 8.5 \times 10^3$ M^{-1} s^{-1}.

Complexation of short-chain polypeptides by nickel(II) enhances the acidity of the amide protons, and as a consequence many nickel(II) complexes have been prepared in water solution that are of square-planar configuration with coordinated imide groups.[1–6] *N,N'*-Diglycylethylenediamine (DGEN) forms a complex of this configuration provided the pH of the solution is 8 or greater.[6] Coordination of DGEN to nickel is through the two terminal amine groups and through the two deprotonated amide nitrogens.

The transfer of Ni(II) and Cu(II) from short-chain polypeptide complexes to other multidentate ligands such as ethylenediaminetetraacetate may proceed through a variety of pathways.[7–9] These routes include solvent assisted, direct replacement, and proton-transfer limited that may or may not be general-acid catalyzed. The variation in reactivity patterns is dependent upon steric interactions within the substrate complex and the replacing ligand in addition to the relative lability of the leaving groups.[10,11]

This study involves the transfer of Ni(II) from *N,N'*-diglycylethylenediamine to triethylenetetramine (trien). The reaction proceeds through trien$_t$-dependent and -independent pathways. The trien$_t$ dependence is not the same as that observed in other systems.

Experimental Section

Diglycylethylenediamine was synthesized by the method of Gill and Cottrell;[12] the melting point of the dihydrochloride salt was 246 °C. A stock nickel solution, 0.0991 M, was prepared from twice-recrystallized $Ni(ClO_4)_2$ and standardized by EDTA titration. Ionic strength was maintained at 0.10 M with $NaClO_4$. Sodium borate was used to maintain constant pH, and the pH values were converted to hydrogen ion concentration with the extended Debye–Hückel relationship.

Solutions of $NiH_{-2}DGEN$ were prepared by dissolving an analytically weighed portion of DGEN in water followed by addition of an aliquot of Ni(II) stock solution. The solution was bubbled with nitrogen to remove dissolved oxygen before the pH was slowly adjusted to a value greater than 9. The solutions were always prepared fresh and kept under nitrogen. A 50% excess of DGEN was maintained.

Triethylenetetramine solutions were prepared from the recrystallized disulfate salt. Standardization was achieved spectrophotometrically, using Cu(II) at pH 4.8 (acetate buffer). These solutions were also kept

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