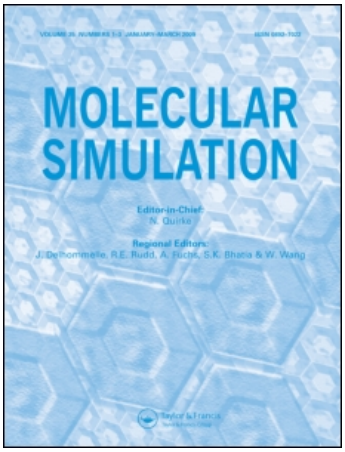

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Polar Solids at High Pressure: NaF

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POLAR SOLIDS AT HIGH PRESSURE: NaF

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Atomistic simulation techniques are used to obtain an equation of state for NaF at elevated temperatures and high pressures: phases with the NaCl and CsCl structures are considered. Two-body potentials and a simple shell model are employed within the quasiharmonic approximation. Calculated and theoretical isotherms and Hugoniots are compared, and other important thermodynamic properties are examined.

KEY WORDS: Polar solids, high pressure, NaF

INTRODUCTION

Atomistic lattice simulations provide an attractive strategy for obtaining the accurate equations of state needed in diverse areas ranging from explosives modelling to the behaviour of systems of geophysical importance. Theoretical studies of ionic solids have largely, if not exclusively, been restricted to zero pressure (see, for example, References 1–3).

In a previous paper [4] we examined in detail the behaviour of MgO (periclase) at high temperatures and pressures (up to ≈ 130 GPa). In the present work the same general approach is used to consider a typical halide – NaF. This system has been well studied experimentally [5–7] and, unlike MgO, clearly undergoes a phase change from rocksalt (fcc) to CsCl (bcc) structures at 20–30 GPa. The characterization of isothermal and isoentropic phase changes serves as a further severe test of any theoretical model. Here we present results for a large number of thermodynamic properties of NaF over extended ranges of temperature and density.

The evaluation of equations of state is essentially a calculation of thermal expansion coefficients and compressibilities. We employ a straightforward, inexpensive methodology using the ionic model, plus the shell model approach to ionic polarization. We work within the well-known quasiharmonic approximation: the vibrational frequencies are harmonic and are functions of the volume but not of the temperature.

It is important to emphasize that only two-body potentials are used to specify the non-Coulombic interactions between the ions.

THEORETICAL METHODS

The theoretical methods employed here are based on those used in a large number of studies of oxides and fluorides at zero pressure (see, for example, References 8–11). The calculations are founded on the ionic model, with charges of $+1$ and -1 assigned to the sodium and fluoride ions, respectively. Electronic polarization effects are incorporated via the shell model due originally to Dick and Overhauser [12] (see also References 13 and 14 for a detailed discussion of its application to lattice dynamics). The associated shell-model polarizability of F^- is 0.99 Å^3.

The two-body potentials, representing the short-range interactions, and the shell-model parameters used in the present work were taken from a recent study of a wide range of ternary fluorides [10] and were obtained using a modified form of the Kim-Gordon electron-gas approach (see References 15–17 for a wide ranging discussion). It is worth emphasizing that previous studies which used these potentials were restricted to zero temperature and pressure. In that our objective is a simple and general procedure, applicable to a large number of materials, we have not attempted any modification or further parameterization of these potentials. The numerical values of the potentials and the shell model parameters are collected in the Appendix.

For a given lattice parameter and temperature the Helmholtz free energy $A(V, T)$ is evaluated directly from the potential energy of the lattice, U_{el}, and the normal mode frequencies, $\nu_j(\mathbf{k})$, for a series of wavevectors $\mathbf{k}$, determined from the dynamical matrix. The Helmholtz free energy is given by

$$A = U_{el} + k_B T \sum_{\mathbf{k},j} \{\tfrac{1}{2}\beta_j(\mathbf{k}) + \ln(1 - \exp[-\beta_j(\mathbf{k})])\}$$

where

$$\beta_j(\mathbf{k}) = \frac{h\nu_j(\mathbf{k})}{k_B T}$$

and k_B is Boltzmann's constant. We sum over the values of $\mathbf{k}$ given by the Chadi–Cohen special points [18].

The pressure, p, is then obtained by differentiation of A, i.e. $p = -(\partial A/\partial V)_T$, and the entropy, S, given by $S = -(\partial A/\partial T)_V$, is calculated directly from the frequencies according to

$$S = k_B \sum_{\mathbf{k},j} \beta_j(\mathbf{k})(\exp[\beta_j(\mathbf{k})] - 1)^{-1} - \ln(1 - \exp[-\beta_j(\mathbf{k})])$$

From these quantities, it is straightforward to obtain an equation of state and any other thermodynamic property of interest by a combination of algebraic manipulation and differentiation. Our procedure differs somewhat from that used by Harding and Stoneham in their calculation of the Hugoniot for NaCl [2]; in particular, we do not work with the Grüneisen constant.

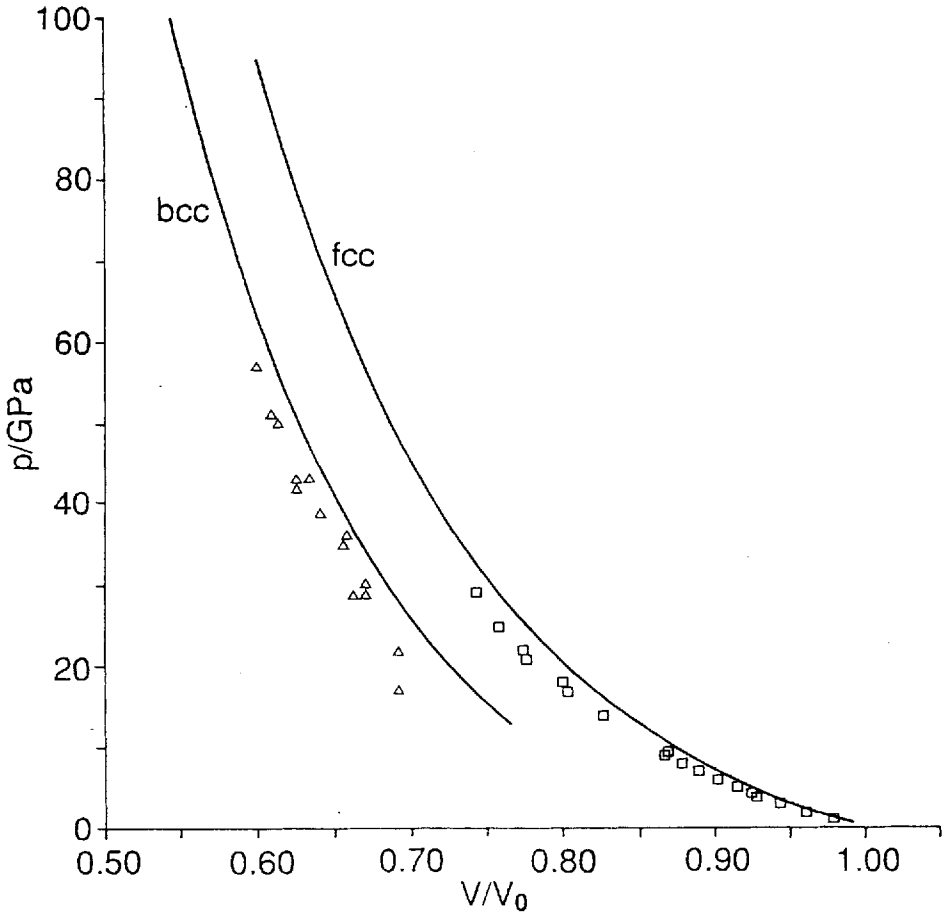

Figure 1 p–V isotherm at 298 K for both the B1 and B2 phases of NaF. The experimental data [6, 19], are marked with crosses for the fcc phase and with open triangles for the bcc phase.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the molar volume with pressure at 298 K for the NaCl (B1) and CsCl (B2) phases. The experimental data of Yagi [19] and Sato-Sorensen [6] are also shown; the agreement is very satisfactory. Our calculated (isothermal) phase transition pressure is 19.7 GPa which compares with experimental values of 23 $\pm$ 3 GPa [6] and 27 $\pm$ 1 GPa [5]. The calculated volume decrease at the transition is 1.17 cm^3/mol, corresponding to a relative volume change of 9.7%; experimental measurements suggest 10.4% [6] and 8.9% [5]. In agreement with Hemley and Gordon [3] we find that the transition pressure decreases with increasing temperature.

The Rankine–Hugoniot relation is of the form

$$U_f - U_i = \tfrac{1}{2}(p_f + p_i)(V_i - V_f)$$

where i labels the undisturbed solid and f labels the solid behind the shock front. Experimentally determined Hugoniot data, in p–V form, are in fact obtained from

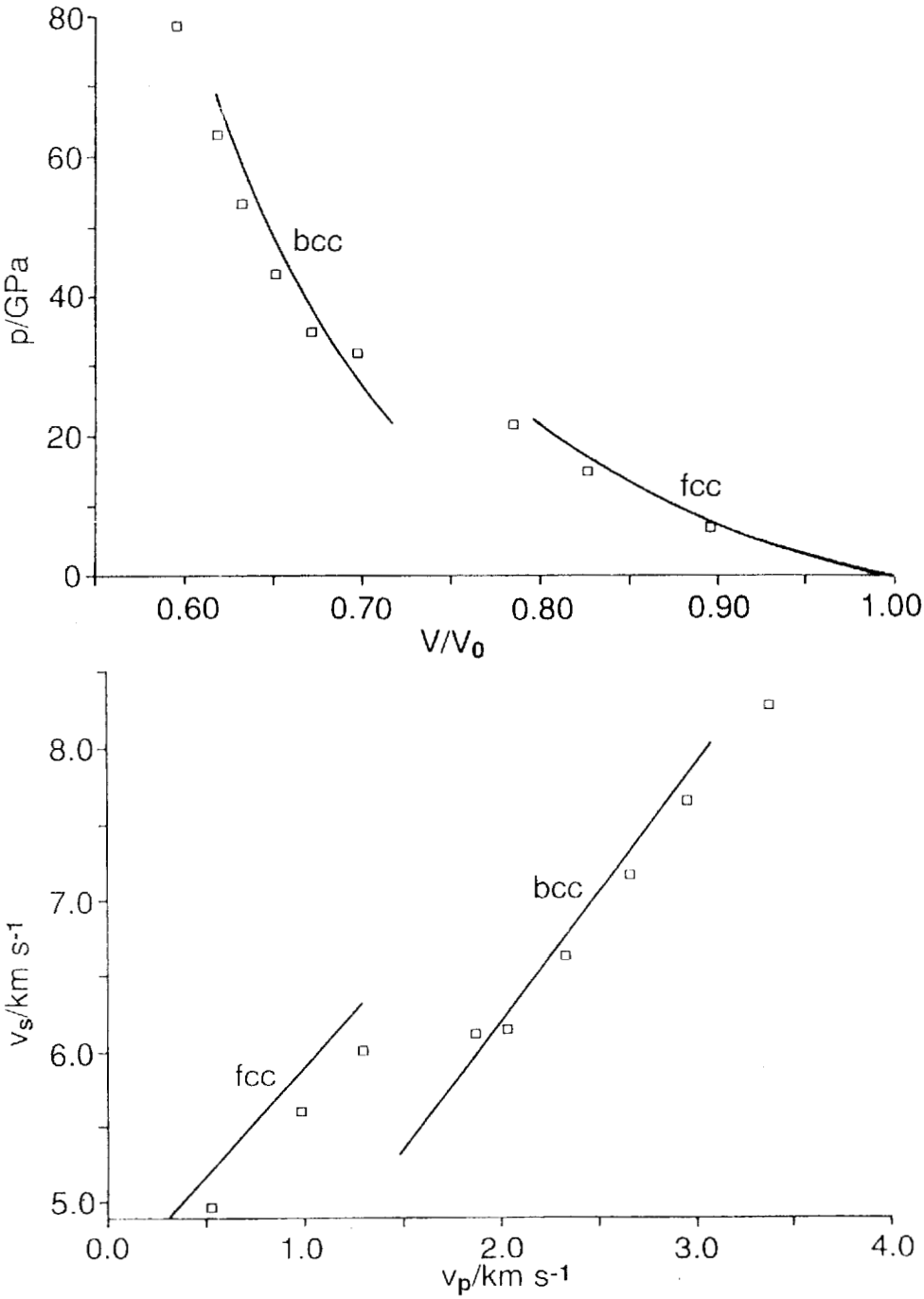

Figure 2 Comparison of calculated Hugoniot data with experimental results, taken from Ref. 7. (a) p–V form. (b) v_s–v_p form.

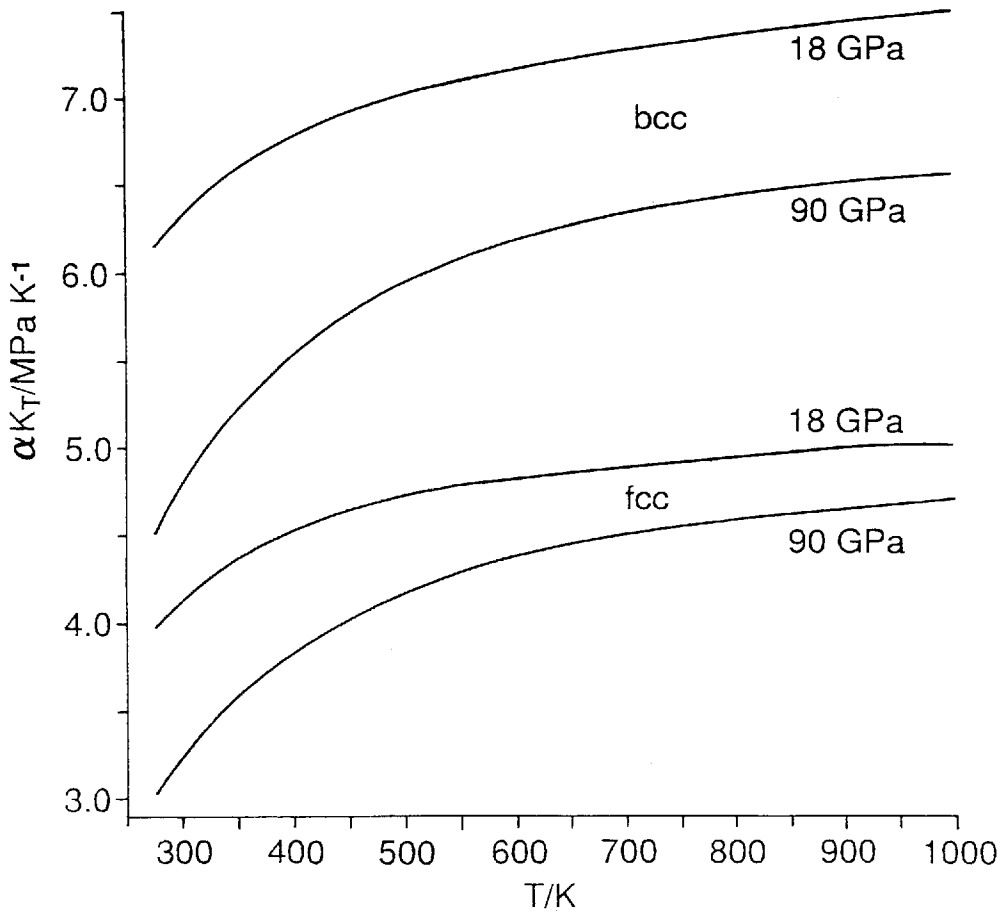

Figure 3 Variation with temperature of the thermal pressure αK_T (in MPa K^{-1}) for both the B1 and B2 phases at pressures of 18 GPa and 90 GPa.

particle (v_p) and shock-wave (v_s) velocities given by

$$v_p = \left[\frac{2(U_f - U_i)}{V_i \rho_i}\right]^{1/2}$$

and

$$v_s = \frac{p_f}{\rho_i v_p}$$

where ρ_i is the initial density of the material. The calculation of Hugoniot trajectories is considered to be a stringent test of interionic potentials [2].

Experimental Hugoniot data [7] are presented in Figure 2 in both p–V and v_s-v_p

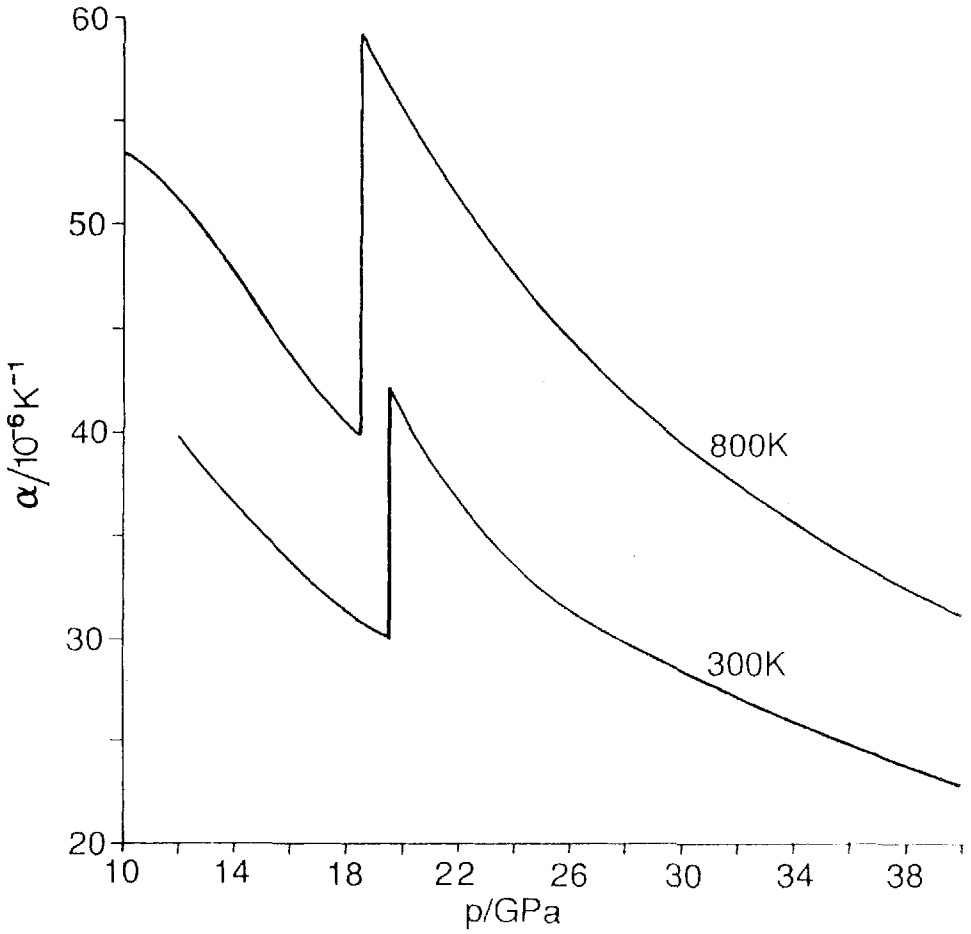

Figure 4 Variation with pressure of the thermal expansion coefficient α (in $10^{-6}\,K^{-1}$) at 300 K and 800 K.

forms, together with those determined from our calculated equation of state. As in the case of the isotherms, theory and experiment agree well. The calculated isoentropic phase change between the B1 and B2 structures is at 19.6 GPa, to be compared with an experimental value of ≈ 24 GPa.

A thermodynamic quantity of considerable interest is the "thermal pressure." The partial derivative $(\partial p/\partial T)_V$ is in fact equal to αK_T, the product of the thermal expansion coefficient and the isothermal bulk modulus. Many approximate models used, for instance, in geophysics, assume that αK_T is independent of the temperature at high T, i.e. that the "thermal pressure" varies linearly with T. Figure 3 illustrates the variation of αK_T with temperature (300–1000 K) for both the B1 and B2 phases at pressures of 18 GPa and 90 GPa. For either phase at 18 GPa, αK_T varies relatively little above moderate temperatures (≈ 500 K).

Lastly, we consider the variation of the calculated thermal expansion coefficient with temperature and volume (see Figure 4). α is approximately proportional to V^t where, at 300 K, $t \approx 4.5$ for fcc and $t \approx 4.8$ for the bcc phase. By way of contrast, the corresponding value for MgO is $t \approx 6.5$ from experimental measurements at this temperature [20] and $t \approx 6.0$ from our earlier calculations [4]. This suggests that a halide such as NaF is not necessarily a good model system for oxides, although this is often assumed. For NaF, the calculated value of α is somewhat larger in the B2 (bcc) phase than in the B1 (fcc) phase. At 300 K, α increases by 40% at the phase transition; the analogous value at 800 K is 49%. Consequently, there is no very marked decrease of α with p for NaF (Figure 4), simply because of the phase change. The geophysical implications of the large value of t for oxides such as MgO have been discussed, for example, by Chopelas and Boelner [21].

CONCLUSIONS

We have used the quasiharmonic approximation to determine a number of thermodynamic properties of NaF over a wide range of elevated temperatures and high pressures. The agreement with existing experimental data is good. As in our previous study of periclase [4], two-body electron-gas potentials appear to be adequate for the high-pressure behaviour of the thermodynamic properties considered here. It has been suggested [22] that "such theories are quite inadequate to explain the equation of states of simple ionic solids"; in the light of the present results, this view appears to be unduly pessimistic.

The quasiharmonic approximation has proved remarkably robust for this application. For sufficiently large interionic distances, the quasiharmonic approximation must break down, leading to striking discontinuities in the temperature variation of calculated properties such as the Helmholtz free energy, A. These separations are close to those characteristic of the fcc phase near its melting point at zero pressure (≈ 1000 K). At any given temperature, larger volumes correspond to lower pressures and so the possible breakdown of the quasiharmonic approximation is less likely at higher pressures (over the same temperature range).

In summary, the simple shell model and two-body potentials used here seem to be very successful at high pressures. The next stage in this investigation is a study of a large number of binary oxides, chlorides and fluorides with analogous phase changes and also an extension of our techniques to systems of lower symmetry.

APPENDIX

The interionic potentials used in this work are listed below, together with the shell model parameters. The potentials are taken to act between the massless shells, and a rational interpolation scheme is used to interpolate between the points as required.

Na^+/Na^+ *R (bohr)*	*E (hartree)*	Na^+/F^- *R (bohr)*	*E (hartree)*	F^-/F^- *R (bohr)*	*E (hartree)*
2.000	0.75578864	0.920	11.12186269	0.401	9.13019033
2.250	0.37263249	1.920	1.23744583	1.401	1.23969212
2.500	0.18048695	2.170	0.73262880	1.651	0.81289709
2.750	0.08601563	2.420	0.43197678	1.901	0.53411711
3.000	0.04037098	2.670	0.25361322	2.151	0.35019838
3.250	0.01865840	2.920	0.14832517	2.401	0.22869181
3.500	0.00847914	3.170	0.08646090	2.651	0.14864295
3.750	0.00377538	3.420	0.05024530	2.901	0.09613038
4.000	0.00163545	3.670	0.02910059	3.151	0.06183752
4.250	0.00067979	3.920	0.01678208	3.401	0.03954115
4.500	0.00026317	4.170	0.00962260	3.651	0.02510865
4.750	0.00008767	4.420	0.00547533	3.901	0.01581200
5.000	0.00001761	4.670	0.00308467	4.151	0.00985727
5.250	−0.00000783	4.920	0.00171621	4.401	0.00606925
5.500	−0.00001531	5.170	0.00094012	4.651	0.00367953
5.750	−0.00001621	5.420	0.00050528	4.901	0.00218730
6.000	−0.00001509	5.670	0.00026526	5.151	0.00126716
6.500	−0.00001251	5.920	0.00013533	5.401	0.00070864
7.000	−0.00001076	6.420	0.00003127	5.901	0.00018349
7.500	−0.00000966	6.920	0.00000554	6.401	0.00001851
8.000	−0.00000891	7.420	0.00000026	6.901	−0.00002065
		7.920	−0.00000039	7.401	−0.00002171
		8.420	0.00000000	7.901	0.00000000

Core and shell charges

Na core	−11.278
Na shell	12.278
F core	0.8981
F shell	−1.8981

Spring constants (in eV Å^{-2})

Na	7982.33
F	51.9528

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