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A solution calorimetric investigation of K–Na mixing in a sanidine–analbite ion-exchange series

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Abstract

Heats of solution have been measured for seven members of a sanidine–analbite ion-exchange series in 20.1 percent HF at 49.7°C under isoperibolic conditions. A cubic least-squares fit to the heat-of-solution data from twenty-eight experiments yields:

$$-\bar{H}_{soln}(\text{kcal/mol}) = 154.411 - 6.233\ N_{Or} + 7.474\ N_{Ab}N_{Or}^2 + 4.117\ N_{Or}N_{Ab}^2$$

where N_{Or} and N_{Ab} are the mole fractions of $KAlSi_3O_8$ and $NaAlSi_3O_8$, respectively. Excess molar enthalpy of K–Na mixing for this series may be expressed as

$$\bar{H}_{ex}(\text{kcal/mol}) = W_{H,Ab}\ N_{Ab}N_{Or}^2 + W_{H,Or}N_{Or}N_{Ab}^2$$

where $W_{H,Ab}$ and $W_{H,Or}$ are the Margules parameters for the enthalpy of K–Na mixing and are equivalent to 7.474 and 4.117 kcal/mol, respectively.

This series of feldspars has a topochemically monoclinic, relatively disordered Al–Si distribution. Comparison of the enthalpy of K–Na mixing for these feldspars with that of a microcline-low albite series of feldspars (Waldbaum and Robie, 1971) having a topochemically triclinic, relatively ordered Al–Si distribution shows that $W_{H,Ab} > W_{H,Or}$ for both; however $W_{H,Ab}$ and $W_{H,Or}$ are 1.8 and 1.0 kcal/mol less, respectively, for the (monoclinic) disordered series than for the (triclinic) ordered feldspars, probably due to a reduction in the strain associated with K–Na substitution in the less dense, disordered feldspar series.

Introduction

In order to characterize the alkali feldspars thermodynamically, it is necessary to obtain enthalpy, entropy, and volume data as functions of both K–Na mixing and Al–Si distribution. Solution calorimetric measurements can provide information on the enthalpy of K–Na mixing and Al–Si exchange. By combining information obtained calorimetrically with data from alkali ion-exchange equilibria (Orville, 1963) information may be obtained on the entropy of K–Na mixing (Thompson and Hovis, in preparation).

In this investigation we have measured heats of solution of a K–Na ion-exchange series of feldspars ranging from sanidine to analbite (as used in the context of Laves, 1952, p. 439; also 1960). This is the first ion-exchange series of feldspars with Al–Si distributions consistent with monoclinic symmetry to be studied calorimetrically. Previously, heats of solution were reported for a triclinic (maximum microcline-low albite) ion-exchange series of feldspars by Waldbaum and Robie (1971). Kracek and Neuvonen (1952) measured heats of solution for various natural feldspars, but not for any ion-exchange series. By comparing the results of the present study with those of Waldbaum and Robie (1971) we now are able to estimate the effects of Al–Si distribution on K–Na mixing properties in the alkali feldspars. This supplements the data of Hovis (1971, 1974), who used the same calorimetric system to determine the enthalpy

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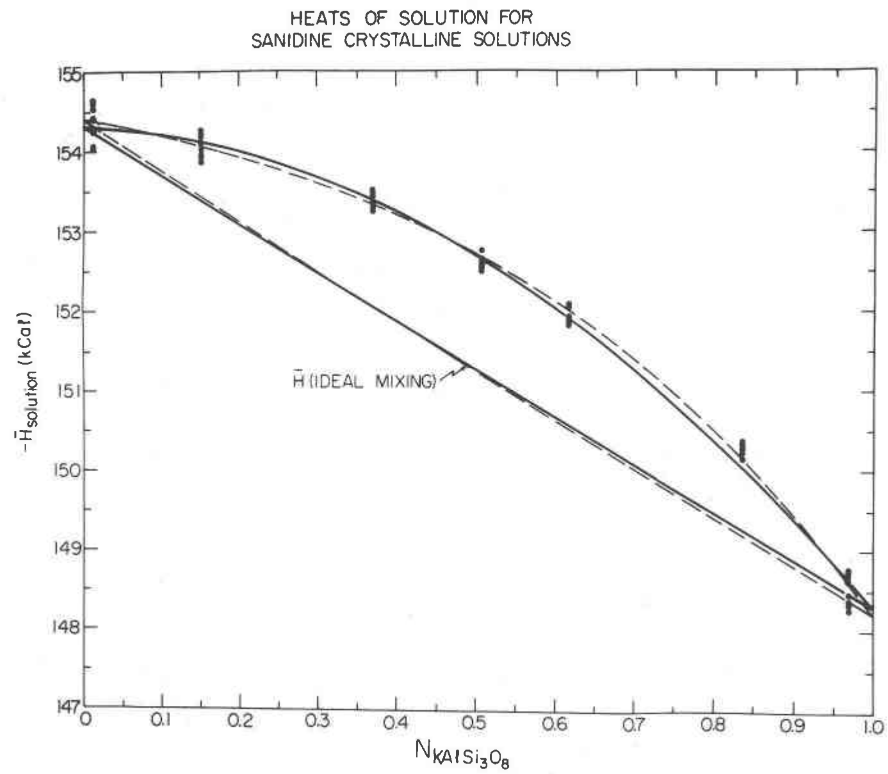

Fig. 1. Heat-of-solution data plotted against composition for sanidine–analbite crystalline solutions. Solid curve represents a quadratic fit [equation (1)] to the data, the dashed curve a cubic fit [equation (2)].

of Al–Si exchange for monoclinic *potassium* feldspars.

Unit-cell dimensions, molar volumes, and chemical compositions for members of this sanidine–analbite series have been reported in the preceding paper (Hovis, 1977; also Hovis and Waldbaum, 1976). Tetrahedral site occupancies for all members of this series are estimated to be $N_{Al(T1)} = 0.271$ and $N_{Al(T2)} = 0.229$ (for nomenclature, see Thompson, 1969, 1970).

Calorimetry

Details of our calorimetric apparatus and procedures have been described elsewhere (Hovis, 1971; 1974, p. 125–127; also see Robie and Hemingway, 1972), and only the most important aspects will be repeated here.

Feldspar crystalline solutions were dissolved in 20.1 weight percent HF (to conform with acid strengths used by previous investigators: King, 1951; Kracek and Neuvonen, 1952; Waldbaum, 1966, p. 18) at 49.7°C (1 atm) under isoperibolic conditions, using an internal sample container (Waldbaum and Robie, 1970). Early experiments were conducted using 940 grams of acid, later ones using 910 grams of acid (Table 1); this had no detectable effect on the resulting heats of solution. Generally, three experiments were conducted using the same acid solution; 0.65 to 1.00 gram of material (−325 mesh) was dissolved during each experiment. This violates the rule of strict stoichiometry (Hovis, 1974, p. 125), but because of the very small amounts of feldspar dissolved, the solutions remained in the ideally dilute range with respect to the ions in solution; this procedure had no detectable effect on the calorimetric results (Hovis, 1974, p. 129).

Thermometry and data reduction are as described by Hovis (1974, p. 126–127; 1971).

Calorimetric results

Calorimetric data for the sanidine–analbite crystalline solutions are shown in Figure 1 and recorded in Table 1. These data represent the results of 28 heat-of-solution experiments on seven different feldspars; two heats of solution are given for most experiments, the first based on the heat capacity of the calorimeter before dissolution, the second on the heat capacity after dissolution. Calorimetric data are not presented

Table 1. Solution calorimetric data for sanidine-analbite crystalline solutions

Feldspar, N_{Or}	Run No.*	Sample Mass (g)	ΔT**	Mean Solution Temperature (°C) - IPTS-68	Heat Capacities (J/deg) Initial	Final	Heats of Solution† at Mean Temperature (J/g)	(kcal/mol)
7015, .0114	177*	1.00260	0.637664	49.467	3875.89	3868.60	2465.28, 2460.27	154.615, 154.301
7015, .0114	178*	1.00440	0.638414	49.687	3879.02	3883.63	2465.77, ---	154.646, ---
7015, .0114	179*	1.00382	0.638203	49.726	3875.39	3863.35	2464.06, 2456.03	154.539, 154.035
7015, .0114	180*	0.64598	0.410756	49.724	3871.99	3868.88	2462.19, 2459.97	154.421, 154.282
7015, .0114	191	0.76397	0.500652	49.912	3756.93	3748.95	2462.17, 2456.64	154.420, 154.073
7059, .1521	225	0.82429	0.533550	49.722	3766.15	3766.32	2437.93, 2437.73	154.221, 154.208
7059, .1521	226	0.80988	0.523881	49.796	3764.42	3760.60	2435.22, 2432.43	154.049, 153.873
7059, .1521	227	0.81425	0.527633	49.748	3755.68	3755.91	2433.83, 2433.67	153.961, 153.951
7059, .1521	250	0.79449	0.514550	49.769	3765.39	3762.22	2438.79, 2436.43	154.275, 154.126
7057, .3711	213	0.82085	0.521685	49.600	3768.32	3762.88	2395.08, 2391.32	153.530, 153.289
7057, .3711	214	0.84360	0.536259	49.854	3766.49	3761.95	2394.45, 2391.25	153.490, 153.285
7057, .3711	215	0.81626	0.518925	49.894	3765.73	3763.17	2394.16, 2392.23	153.471, 153.348
7057, .3711	246	0.82435	0.524839	49.806	3760.86	3757.82	2394.59, 2392.36	153.499, 153.356
7044, .5091	188*	0.75854	0.462019	49.807	3876.30	3874.69	2361.15, 2359.91	152.609, 152.530
7044, .5091	189*	0.76378	0.465354	50.039	3876.64	3874.51	2362.06, 2360.51	152.669, 152.568
7044, .5091	190*	0.76592	0.474852	49.731	3812.58	3807.30	2363.84, 2360.30	152.783, 152.554
7044, .5091	258	0.79440	0.498062	49.828	3766.02	3765.78	2361.30, 2360.86	152.619, 152.591
7058, .6183	216	0.81949	0.507990	49.830	3767.19	3765.83	2335.38, 2334.24	151.926, 151.852
7058, .6183	217	0.78932	0.489193	50.020	3768.49	3766.90	2335.73, 2334.47	151.949, 151.867
7058, .6183	262	0.84802	0.526452	49.889	3765.73	3766.41	2337.92, 2338.04	152.091, 152.100
7060, .8358	228	0.81682	0.494748	49.653	3765.67	3762.74	2281.02, 2278.97	150.300, 150.165
7060, .8358	229	0.80487	0.487804	49.912	3763.43	3764.86	2281.02, 2281.62	150.300, 150.340
7060, .8358	253	0.76938	0.466059	49.795	3767.32	3764.27	2282.21, 2280.11	150.379, 150.240
7036, .9691	181*	0.79032	0.456729	49.656	3875.85	3861.37	2239.99, ---	148.747, ---
7036, .9691	183*	0.80916	0.468002	49.723	3869.57	3862.25	2238.21, 2233.73	148.628, 148.331
7036, .9691	184*	0.80169	0.463723	49.724	3872.71	3860.48	2240.22, 2232.90	148.762, 148.276
7036, .9691	204	0.79946	0.474424	49.851	3767.71	3765.62	2236.00, 2234.51	148.482, 148.383
7036, .9691	248	0.80005	0.476641	49.738	3758.36	3757.46	2239.23, 2238.43	148.696, 148.643

* An asterisk after the run number indicates runs carried out in 940 grams of acid solution. All other runs were carried out in 910 grams of acid.

**Temperature change during dissolution corrected for heat exchange (°C).

† The two heats of solution for each run result from calculations based on heat capacities determined for the calorimeter vessel before ("initial Cp") and after ("final Cp") dissolution. Both heats of solution from every run were used in least-squares analyses of the data.

for the small number of runs where heat capacities were associated with either abnormally high or low α-values, because such data are considered unreliable. Values of α are calculated during each calorimetric experiment and indicate the rate at which heat exchange between the reaction vessel and its surroundings changes with temperature during an experiment (Waldbaum, 1966). Abnormal α-values may be indicative of problems, such as failure of an experiment to go to completion, and are one criterion used to evaluate a run.

Heat-of-solution values (Table 1) expressed in joules/gram are independent of the assumed feldspar chemical composition. Values given in kcal/mol (where 1 defined calorie = 4.184 joules) are based on atomic weights corresponding to the compositions stated in the preceding paper (Table 3) and assuming such compositions are precisely on the $(K,Na)AlSi_3O_8$ join. No corrections were made for minor-element content; as stated in the preceding paper, these elements were present in very small amounts and should be nearly constant for all members of the ion-exchange series.

Least-squares fits to the data in Table 1 as a function of N_{Or} (mole fraction of $KAlSi_3O_8$) yield the following quadratic and cubic equations:

$$-\bar{H}_{soln}(\text{kcal/mol}) = 154.326(\pm.008) - 6.033(\pm.010)N_{Or} + 5.691(\pm.035)N_{Or}N_{Ab} \quad (1)$$

and

$$-\bar{H}_{soln}(\text{kcal/mol}) = 154.411(\pm.008) - 6.233(\pm.013)N_{Or} + 7.474(\pm.085)N_{Ab}N_{Or}^2 + 4.117(\pm.080)N_{Or}N_{Ab}^2 \quad (2)$$

(To convert heats of solution to units of kilojoules/mol, multiply the coefficients by 4.184.) Curves corresponding to these equations are plotted in Figure 1 along with the line for "ideal" mixing based on mechanical mixtures of end-member feldspars. The standard deviation of equation (1) is ±0.17 kcal/mol and of equation (2) is ±0.16 kcal/mol. Thus, statistically the cubic fit is better than the quadratic one, but by a very small, probably insignificant margin, considering the precision of the individual runs. Nevertheless, the cubic fit may be more realistic when considering the physical significance of the data.

Effect of sample inhomogeneity on calorimetric results

Sample inhomogeneity (Hovis, 1977) has an effect on heats of solution in any chemical system where heats of mixing exist. In such a system, a set of mechanical mixtures about the mean composition would result in a lower absolute value for heat of mixing than would a single homogeneous phase. However, if the mechanical mixture represents a relatively small range of chemical compositions, the effect of inhomogeneity should be small, perhaps negligible.

Of the five feldspars with intermediate chemical compositions, four were inhomogeneous to a minor extent, with ranges of ±3.5 mole percent Or or less. Feldspar 7057 was somewhat more inhomogeneous, with a range of ±11 percent. It is impossible to make rigorous corrections for inhomogeneity without detailed quantitative information about *how much* of each composition is represented in each of the feldspar samples. However, it is possible to estimate the maximum effect that inhomogeneity would have on the heats of solution. This can be done by assuming that each sample is made up of a mechanical mixture of two feldspars, *one at each end of the composition range of each feldspar.* Based on equation (1) or equation (2), we may then calculate the heat of solution for a 50:50 mechanical mixture of these two feldspars and compare it with the actual heat of solution for a feldspar in the middle of the composition range. Doing this for feldspars 7059, 7044, 7058, and 7060, we find that the *maximum* effect on the heats of solution would be approximately 0.01 kcal/mol. Because each feldspar crystalline solution does *not* consist of a mechanical mixture of two feldspars at either end of the composition range, but rather a whole series of phases along the entire range, any correction to the heats of solution of these four feldspars should be even less than 0.01 kcal/mol; in the present study this is negligible.

Inhomogeneity in sample 7057 was somewhat more serious than in the other samples. Estimating the effect of inhomogeneity in this sample as above indicates an effect of 0.08 kcal/mol. However, this too would be the maximum effect, since this feldspar consists of a whole range of compositions, not just two.

In order to check the maximum effect that inhomogeneity could have on the calculations, least-squares fits to heats of solution were performed after adding 0.08 kcal/mol to the values of $-\bar{H}_{soln}$ for sample 7057 and 0.01 kcal/mol to the values of $-\bar{H}_{soln}$ for all other feldspars except the end members. These calculations resulted in a change of the last coefficient in equation (1) to 5.848 (±.035) kcal/mol and of the last two coefficients in equation (2) to 7.357(±.090) and 4.516(±.080) kcal/mol, respectively.

Comparison of calorimetric data with those of other investigators

The heat-of-solution values for sanidine and analbite may be compared with those of Waldbaum and Robie (1971), who measured the heats of solution of nearly identical end-member samples but used a different HF solution calorimetric data acquisition system. Their values are between 1 and 2 kcal/mol different from the present data, not only for sanidine and analbite, but also for microcline and low albite. Therefore, differences between the two sets of calorimetric measurements are probably systematic. Each system yields internally consistent results, and enthalpy changes due to compositional variations or changes in Al–Si distribution in alkali feldspars are the same as measured on either system. Therefore, the results from either calorimetric system can be considered valid, but at present *absolute values* of

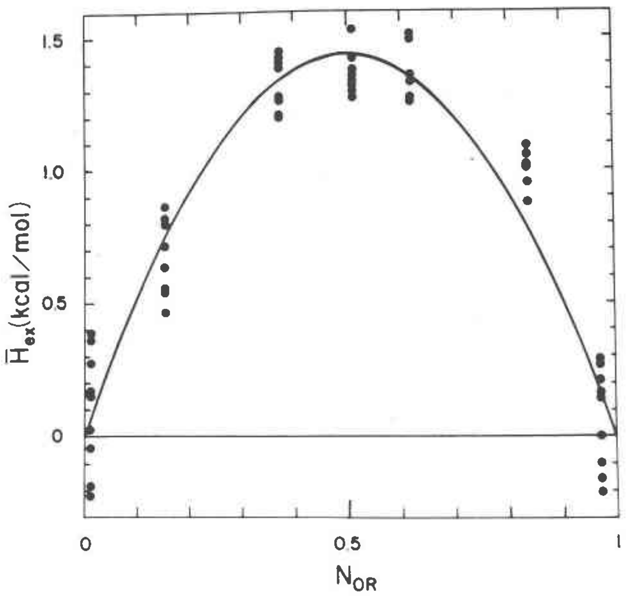

Fig. 2a. Excess molar enthalpy plotted against composition. Curve corresponds to equation (3). Data points are relative to the line of "mechanical mixtures" based on equation (1).

heats of solution from the two systems should not be used interchangeably.

Excess mixing properties of sanidine-analbite crystalline solutions

The excess enthalpy due to K–Na mixing is equal to the difference between the quadratic formulation

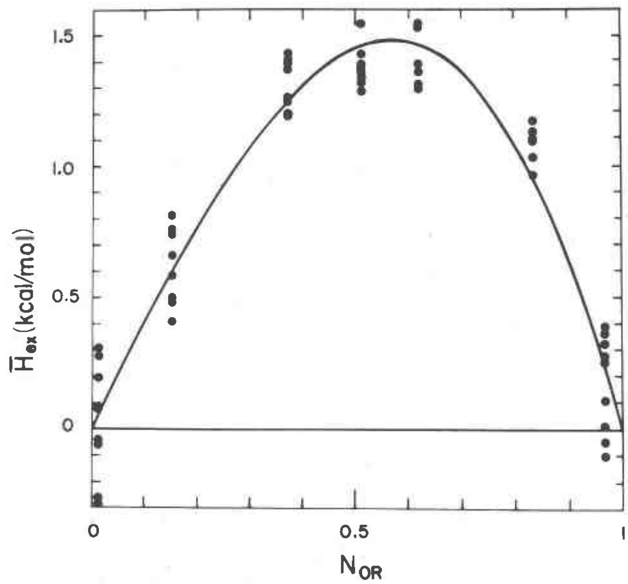

Fig. 2b. Excess molar enthalpy plotted against composition. Curve corresponds to equation (4). Data points are relative to the line of "mechanical mixtures" based on equation (2).

given by equation (1), or the cubic expression of equation (2), and the associated line corresponding to mechanical mixtures of end-member feldspars. For the sanidine–analbite series of the present investigation, equations of $\bar{H}_{ex}$ corresponding to equations (1) and (2) above are

$$\bar{H}_{ex}(\text{kcal/mol}) = 5.691(\pm.035)N_{Or}N_{Ab} \quad (3)$$

and

$$\bar{H}_{ex}(\text{kcal/mol}) = 7.474(\pm.085)N_{Ab}N_{Or}^2 + 4.117(\pm.080)N_{Or}N_{Ab}^2 \quad (4)$$

Curves corresponding to equations (3) and (4) are plotted in Figures 2a and 2b.

Excess molar volume data for the same feldspar series are given in the preceding paper [Hovis, 1977, equation (7)]. Using the thermodynamic relationship, $\bar{E}_{ex} = \bar{H}_{ex} - P\bar{V}_{ex}$ (Thompson, 1967), we can develop general expressions for excess internal energy of K–Na mixing:

$$\bar{E}_{ex}(\text{kcal/mol}) = (5.691 - 0.0862P)N_{Or}N_{Ab} \quad (5)$$

and

$$\bar{E}_{ex}(\text{kcal/mol}) = (7.474N_{Or} + 4.117N_{Ab} - 0.0862P)N_{Or}N_{Ab} \quad (6)$$

where pressure is expressed in kilobars. For pressures up to 10 kbar and more, the excess enthalpy and internal energy of K–Na mixing are virtually identical, owing to the very small value of W_V, the Margules parameter for molar volume.

Excess mixing properties as functions of Al–Si distribution for alkali feldspars

Excess internal energies of mixing for the low albite–microcline ion-exchange series investigated by Waldbaum and Robie (1971) and also for the analbite–sanidine series of the present study are recorded in Table 2. Because differences in the mixing properties for the two series are the combined result of changes in Al–Si distribution over *four* tetrahedral sites, it is impossible to factor these heat-of-solution differences into effects due to changes in the Al–Si population of each site. However, we can make some general comments about K–Na mixing properties in alkali feldspars as a whole:

(1) Excess internal energy and enthalpy are positive for all alkali feldspar ion-exchange series, regardless of Al–Si distribution.

(2) $W_{H,Ab} > W_{H,Or}$ (and $W_{E,Ab} > W_{E,Or}$) for asymmetric fits to the heat-of-solution data of ordered and disordered ion-exchange series.

(3) $W_{E,\text{Ab}}$ and $W_{E,\text{Or}}$ are 1.8 and 1.0 kcal/mol less, respectively, for the (topochemically monoclinic) disordered series than for the (triclinic) ordered series of feldspars, based on the cubic fits to heat of solution data. W_E is 1.4 kcal/mol less for the disordered series, based on the quadratic fits to the same data.

Interpretation of the results

Asymmetry of the heats of K–Na mixing in the alkali feldspars is probably related to strain created by the substitution of ions of unequal size into the "*M*" crystallographic position in the structures of these minerals. In both of the alkali feldspar series studied calorimetrically, the heat effect resulting from the substitution of a potassium ion into a sodic feldspar (reflected by the value of the Margules parameter, $W_{H,\text{Ab}}$) is greater than that resulting from the substitution of a sodium ion into a potassic feldspar (reflected by $W_{H,\text{Or}}$). Put simply, less strain is created when a small ion occupies a cavity than when a relatively large ion occupies the same (or a slightly smaller) cavity.

Differences in the K–Na mixing properties between topochemically monoclinic, disordered and topochemically triclinic, ordered alkali feldspars can also be explained as a function of strain. The disordered feldspars have slightly greater molar volumes (Orville, 1967; Hovis, 1971 and 1974), and therefore lower densities, than more ordered compositionally-equivalent feldspars. Because their structures are more open, the strain created by ionic substitution of potassium and sodium ions in the "*M*" crystallographic position is not as great as in the relatively ordered feldspars. The less strain, the smaller the effect of K–Na mixing.

A more detailed analysis of these results will be given in a later report (Thompson and Hovis, in preparation), where excess enthalpy and excess molar volume data are combined with data based on Orville's (1963) ion-exchange experiments (Thompson and Waldbaum, 1968) to give excess entropy relationships for sanidine–analbite crystalline solutions.

Table 2. Internal energies of K–Na mixing at 1 atm for feldspar crystalline solutions

Feldspar Series	$W_{E,\text{Or}}$ (kcal/mol)	$W_{E,\text{Ab}}$ (kcal/mol)	$\bar{E}_{ex/50:50}$ (kcal/mol)
Low albite - microcline (Waldbaum and Robie, 1971, asymmetric or cubic fit to the data)	5.928 ±.085	8.457 ±.099	1.798
Low albite - microcline (Waldbaum and Robie, 1971, symmetric or quadratic fit to the data)	7.075 ±.044	7.075 ±.044	1.768
Analbite - sanidine (This investigation, asymmetric or cubic fit to the data)	4.117 ±.080	7.474 ±.085	1.449
Analbite - sanidine (This investigation, symmetric or quadratic fit to the data)	5.691 ±.035	5.691 ±.035	1.423

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