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The specific heat of Al-based compounds, evaluation of the Neumann-Kopp rule and proposal for a modified Neumann-Kopp rule

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Abstract

The application of the Neumann-Kopp rule to aluminum containing compounds produces a kink in the specific heat caused by the description of pure aluminum in the SGTE Unary database. Two ways to get rid of this problem are investigated. In a first step, we tried to redefine the description of aluminum above its melting point using a reverse Neumann-Kopp approach. After a systematic review of the experimental  $C_p$  data for all the aluminum based compounds, we could evaluate the accuracy of the Neumann-Kopp rule. We could find a nearly systematic overestimation of the  $C_p$  of the order of 15 %. This makes the use of the reverse Neumann-Kopp approach inapplicable. In a second step, based on this analysis of the available data, we propose another approach consisting in defining the  $C_p$  of a compound by a composition average of the  $C_p$  of the pure elements, not at the same temperature as in the Neumann-Kopp rule, but rather at a temperature normalized to the melting point of each pure element and the compound. Not only are the results in much better agreement with the experimental data than the conventional Neumann-Kopp rule, but also, there is no longer a need to define the  $C_p$  of aluminum above its melting point.

Keywords:

specific heat; heat capacity; Neumann-Kopp; aluminum

## 1. Introduction

In the SGTE Unary database the  $C_p$  of *fcc* aluminum is defined below and above the melting point. Above the melting point, the so-called SGTE extrapolation [1, 2] is used, characterized by a convergence of the  $C_p$  of the solid towards that of the liquid phase. This results in a kink on the  $C_p$  curve. For the modeling of intermetallic compounds in the Calphad approach, in the absence of experimental or calculated  $C_p$  data, the Neumann-Kopp Rule (NKR) is often used. It consists in estimating the  $C_p$  at a given temperature by a composition average of those of the constituting elements at the same temperature. Due to the SGTE estimation, the calculated  $C_p$  of aluminum-based compounds modeled with the NKR always presents a kink at the melting point of aluminum which is unphysical.

This emphasizes the need to define the  $C_p$  for pure *fcc* aluminum above its melting point. This has been done previously for example by using calculated DFT data [3]. In the present work, the

possibility to use experimental data through a reverse NKR approach is investigated. Available experimental specific heat data of aluminum binary compounds have been systematically scanned from the literature. From the knowledge of the  $C_p$  of the second element and the composition of the compound, it should be possible to deduce an effective  $C_p$  for aluminum using the reverse NKR. Results will be presented, and the effectiveness of this approach will be discussed. Finally, a modified NKR using normalized temperatures will be proposed.

## 2. NKR, achievements and problems

As detailed by Schick *et al.* [4], the NKR [5] consists in estimating the heat capacity of an unknown compound at a given temperature by a composition average of the constituent components at the same temperature. Note that this approximation has long been subjected to severe criticisms [6, 7]. Originally [5], the rule was proposed per unit of mass and for the room temperature heat capacity, but it was later extended to mole fraction and to any temperature by taking the heat capacities of the components at the temperature at which one wants to estimate the heat capacity of the compound. It is useful to get an estimate of the heat capacity of a compound when no experimental measurement is available, in particular as a function of temperature.

It is usually written as:

$$C_p^{Ax_A Bx_B}(T) = x_A C_p^A(T) + x_B C_p^B(T) \quad (1)$$

Since:

$$C_p(T) = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{p, N_i} \quad (2)$$

Then:

$${}^0 G^{Ax_A Bx_B}(T) = x_A {}^0 G_A(T) + x_B {}^0 G_B(T) + a + bT \quad (3)$$

which represents a very simple expression for the Gibbs energy in which it is advantageous to refer to pure elements and in which  $a$  and  $-b$  may be easily identified as the enthalpy and entropy of formation of the compound from the pure elements in the given reference state. A deviation to NKR may even be introduced by adding other terms to the equation. A consequence of this equation is that enthalpies and entropies are both independent of temperature.

Of course, if  $C_p$  data exist, a proper stand-alone assessment of the  $C_p$  function of the compounds should be the very first step in a thermodynamic optimization. However, the relation (3) is widely used in the Calphad approach and most published thermodynamic assessments use it. One of the reasons is that the  $C_p$  of the pure elements (and Gibbs energy functions) have been evaluated reliably and are compiled in databases (in the following we will use the SGTE Unary database PURE 5.2 for the calculations [8]). Another reason is that, with a stand-alone description of the compounds, much more parameters are needed that cannot be adjusted if no sufficient explicit  $C_p$  data exists. This approach therefore allows to predict many compounds like borides [9] or oxides [10]. quite nicely. An additional consideration arises regarding the structure of the component that should be used. To avoid strong discontinuities, one generally takes the structure of the compound at room temperature (the Standard Element Reference SER) whatever the temperature even if the element is not stable in this crystal structure at said temperature. For example, the  $C_p$  of a compound containing titanium will be evaluated using the  $C_p$  of *hcp* titanium even in the temperature range where *bcc*

titanium is stable. When the reference phase is magnetic, the  $C_p$  of the non-magnetic phase is used. For example, the  $C_p$  of an iron-based compound will be evaluated from the  $C_p$  of a non-magnetic *bcc* phase (note that, in this case,  $a$  and  $-b$  no longer represent the enthalpy and entropy of formation from the pure elements in their reference state).

Another option is to take the structure of the element comparable to the site-specific arrangement in the compound. For example, if the element has a high coordination number (CN) in the compound, one may prefer to take the  $C_p$  of the *bcc* structure (CN 14) preferably to that of the *fcc* structure (CN 12). Note that this is, in practice, of limited consequence because the  $C_p$  of both structures are often taken as equal in databases.

A problem arises if a compound is stable at a temperature higher than the melting point of at least one of the components. In such cases, one should rely on the  $C_p$  of the element in the used solid crystal structure extrapolated above the melting point. Here, the so-called SGTE extrapolation comes into play, where the aim is to extrapolate the  $C_p$  of the solid phase above the melting point of the pure element. It consists in making the  $C_p$  of the solid phase above its melting temperature converge towards that of the liquid phase. This avoids a restabilization of the solid phase at very high temperatures because a simple extrapolation of the  $C_p$  curve of the solid would lead to a very large (and therefore stabilizing)  $C_p$  at high temperature. The well-known problem of this approximation is that it creates a kink in the  $C_p$  curve at the melting point for several elements having a  $C_p$  of the solid at the melting point higher than that of the liquid [4]. This evidently has repercussions on the calculated  $C_p$  of any compound estimated with the NKR.

The most typical example of the problems caused by these two approximations is the estimation of the  $C_p$  of aluminum containing compounds (see Fig. 1 as an example). It has been reported many times, see *e.g.* Refs. [3, 4]. The reason is twofold, because aluminum presents two complications: *i*) a low melting point, which means that many compounds have higher melting points and *ii*) the fact that the  $C_p$  of aluminum at its melting point is much higher than that of liquid aluminum (this is not the case for Ni shown in the same figure). This has been attributed to the presence of different contributions to the  $C_p$  of pure *fcc* Al (quasi-harmonic, electronic) and, in particular, to thermal vacancies [3, 11, 12]. This results in a very strong kink for this specific element, which would not necessarily be a problem for pure aluminum if it did not also produce a kink on the calculated  $C_p$  of aluminum containing compounds because of the NKR. There is evidently no reason that the  $C_p$  of the AlNi compound, as in our example, keeps a trace of the melting point of pure aluminum. Note that a kink is also present at the melting point of nickel, so that the problem is more general than Al-containing compounds.

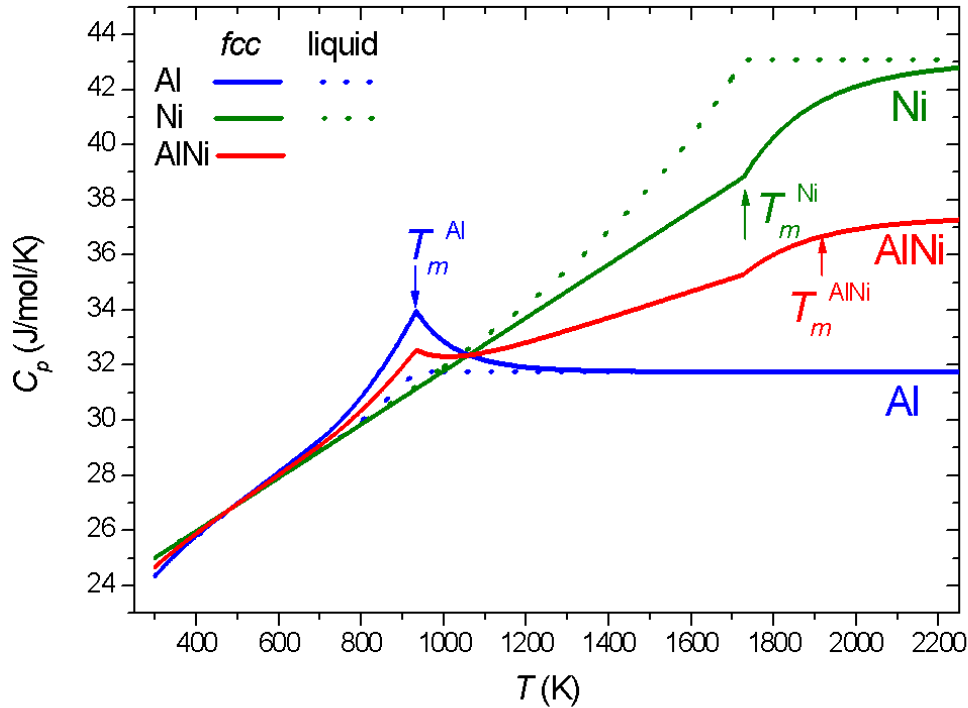


Fig. 1. Calculated  $C_p$  of fcc and liquid Al, nonmagnetic fcc and liquid Ni and the AlNi compound as estimated by the NKR.

Different solutions to this problem have been considered in the literature to cope with this problem, see the discussion in paragraph 4.3.

The idea we would like to evaluate in the present work is the following: if NKR efficiently predicts the  $C_p$  of compounds in the low temperature region where aluminum has its  $C_p$  well defined, then the  $C_p$  of fcc Al at temperatures above the melting point of fcc Al could be evaluated from the information on the  $C_p$  of the aluminum containing compounds when measured at temperatures above the melting point of aluminum, given that one knows the  $C_p$  of the other constituent. This is the principle of what we call the reverse NKR.

A point in favor for this method is that a lot of compounds exist with a melting point higher than pure aluminum, including compounds rich in aluminum, which potentially allows a more precise extrapolation towards pure aluminum. Also, there are many systems with several stable compounds at different compositions, which allows to anticipate the trend of the variation of the  $C_p$  as a function of composition in the whole composition range from a pure element to pure aluminum.

### 3. Results

Only binary compounds have been searched for in the literature and only the experimental  $C_p$  data above room temperature have been collected (for many compounds only their low temperature  $C_p$  is reported, in relation to their physical properties). From our systematic search, experimental  $C_p$  data were found in 24 Al–X systems ( $X=Ag, As, B, C, Ca, Ce, Co, Cr, Cu, Er, Eu, Fe, La,$

N, Nb, Nd, Ni, P, Pr, Sb, Sc, Ti, Yb, Zr). The collection of all the digitized data is reported in Supplementary Materials. The original data can be found in Refs. [6, 13-48]. Figs. 2 to 6 present a collection of representative systems.

### 3.1. Verification of the validity of the NKR

The first thing to verify before applying the reverse NKR technique is the validity of the NKR itself in the temperature range where there is no uncertainty concerning the  $C_p$  of both constituting elements. This is typically for temperatures lower than the melting point of aluminum. One can easily see from Figs 2 to 6 and from the figures in the Supplementary Materials that there is a quasi-systematic deviation from the NKR. The reported experimental data are generally lower than the  $C_p$  expected from the NKR by -2 to -4 J/mol/K. Exceptions are found for  $\text{Ag}_2\text{Al}$ ,  $\text{Ag}_3\text{Al}$ ,  $\text{Al}_4\text{C}_3$  and  $\text{Al}_{30}\text{Ce}_{70}$  for which a perfect agreement is observed, and AlAs for which a higher  $C_p$  is observed compared to the NKR. Note that the  $C_p$  of ytterbium has a very strange behavior that may indicate an error in the SGTE Unary database PURE 5.2. When data is available for several compounds in the same system, one can check whether a systematic increase or decrease of the  $C_p$  is observed. Several systems deserve particular attention due their complexity or the high amount of available data and are therefore described in the following.

### 3.2. Al–Cu

The  $C_p$  is more or less well predicted in this system for the different intermetallic compounds. However, the predicted trend as a function of Al composition *i.e.* an increase with increasing Al content is not supported by the data, in particular for the compounds  $\text{Al}_{13.8}\text{Cu}_{86.2}$  which has the highest and  $\text{Al}_{66}\text{Cu}_{34}$  which has the lowest  $C_p$ .

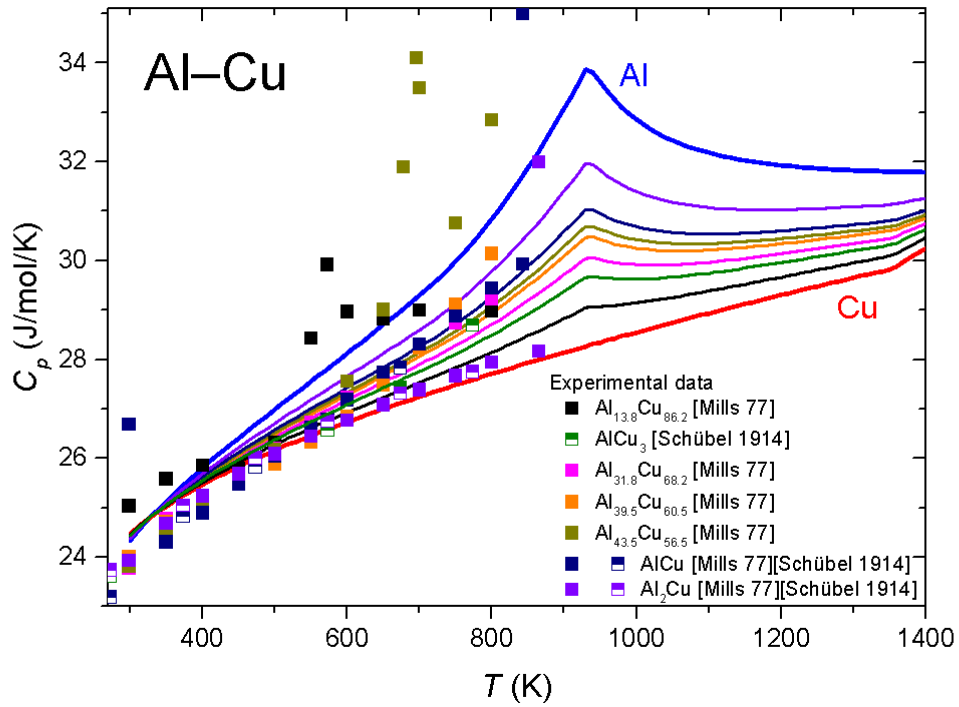


Fig. 2. Experimental and calculated (NKR, lines)  $C_p$  data in Al–Cu system. Pure elements from the SGTE Unary database are shown for comparison. Same colors are used for points and curves.

### 3.3. Al–Ni

For  $\text{AlNi}_3$ , there is a strong discrepancy between the measurement of Piatkowski *et al.* [39] and Kovalev *et al.* [22]. If the measurement of Piatkowski *et al.* is preferred, then there is a smooth increase in  $C_p$  as a function of Al concentration going from  $\text{AlNi}_3$  to  $\text{AlNi}$  (note that the different measurements for this latter phase are in good agreement),  $\text{Al}_3\text{Ni}_2$  and then  $\text{Al}_3\text{Ni}$  (also good agreement between different datasets). However, this behavior is not expected from the NKR because Al and (non-magnetic) Ni have similar  $C_p$ . Additionally, the predicted  $C_p$  is always too large.

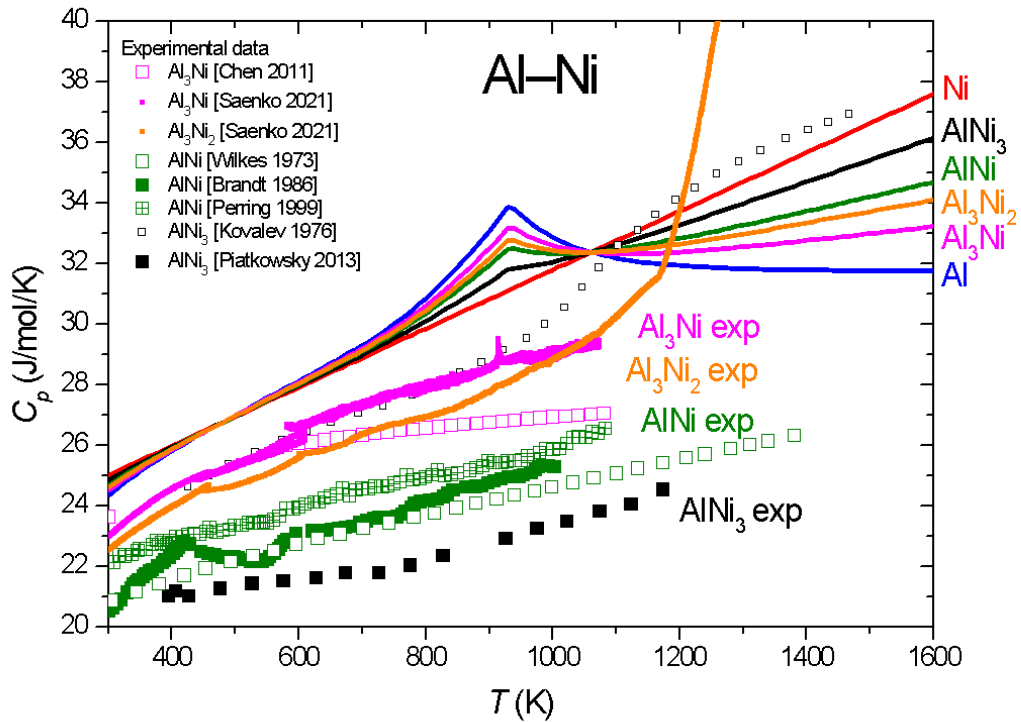


Fig. 3. Experimental and calculated (NKR, lines)  $C_p$  data in Al–Ni system. Pure elements from the SGTE Unary database are shown for comparison. Same colors are used for points and curves.

### 3.4. Al–Fe

This system is interesting because it contains many intermetallic compounds and most of them have been measured accurately. In the low temperature region *i.e.* far from the magnetic transitions of the compounds (that produce large increase of the  $C_p$ ), if neglecting the very low values of Piatkowski *et al.* for  $\text{Al}_{36}\text{Fe}_{64}$  [39], a general decrease of the  $C_p$  is observed as a function of Al concentration. As in the case of the Al–Ni system, no changes could be expected from the NKR since the  $C_p$  of Al and (non-magnetic) iron are also very similar. Predicted values are too large for Al-rich compounds and too low for Al-poor compounds.



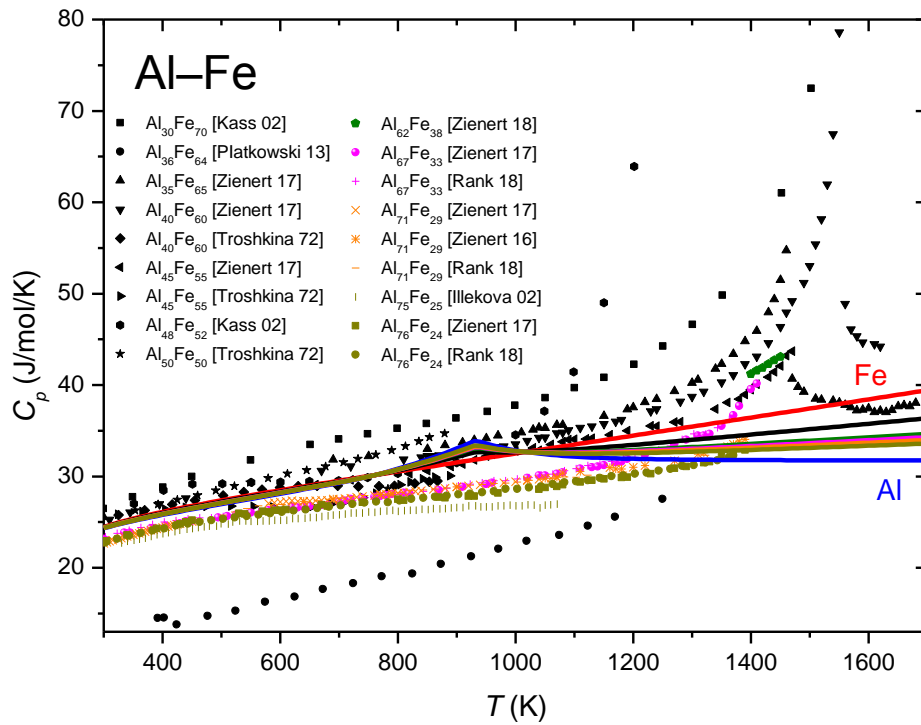


Fig. 4. Experimental and calculated (NKR, lines)  $C_p$  data in Al-Fe system. Pure elements from the SGTE Unary database are shown for comparison. Same colors are used for points and curves.

### 3.5. Al-Ti

In this system the predicted  $C_p$  decrease as a function of Al composition is reproduced by the data (if the measurement of Piatkowski *et al.* is again neglected [39]). Except for AlTi<sub>3</sub>, the predicted  $C_p$  values are too large.

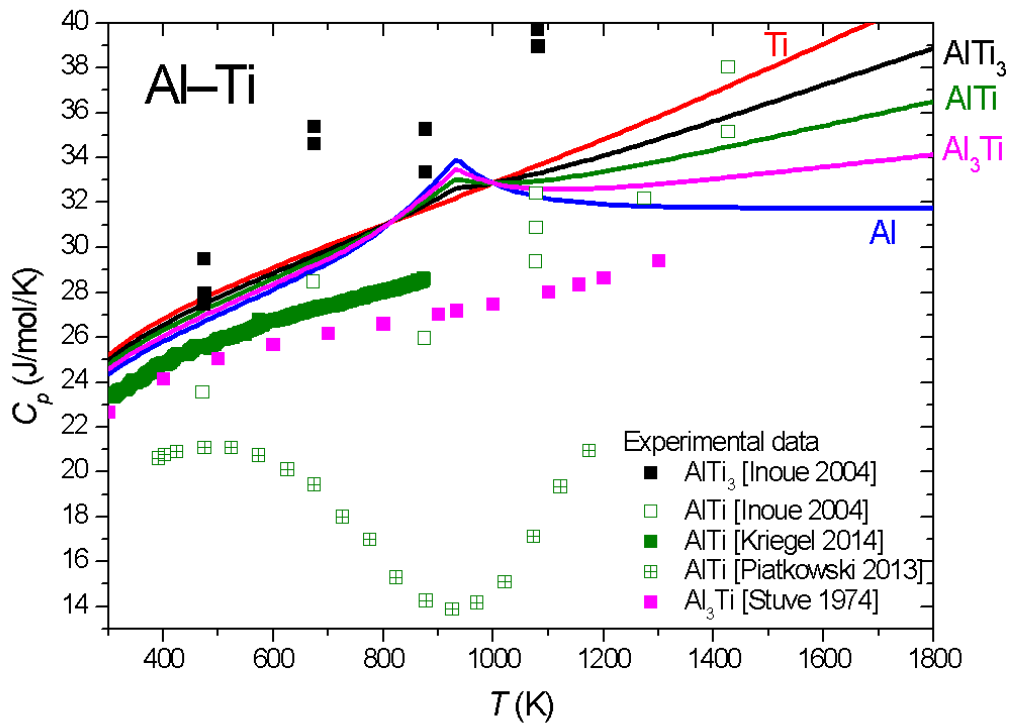


Fig. 5. Experimental and calculated (NKR, lines)  $C_p$  data in Al–Ti system. Pure elements from the SGTE Unary database are shown for comparison. Same colors are used for points and curves.

### 3.6. Al–Zr

For this system, it is difficult to see a trend between the different data but what can be observed in any case is that the calculated  $C_p$  are much larger than the experimental ones.

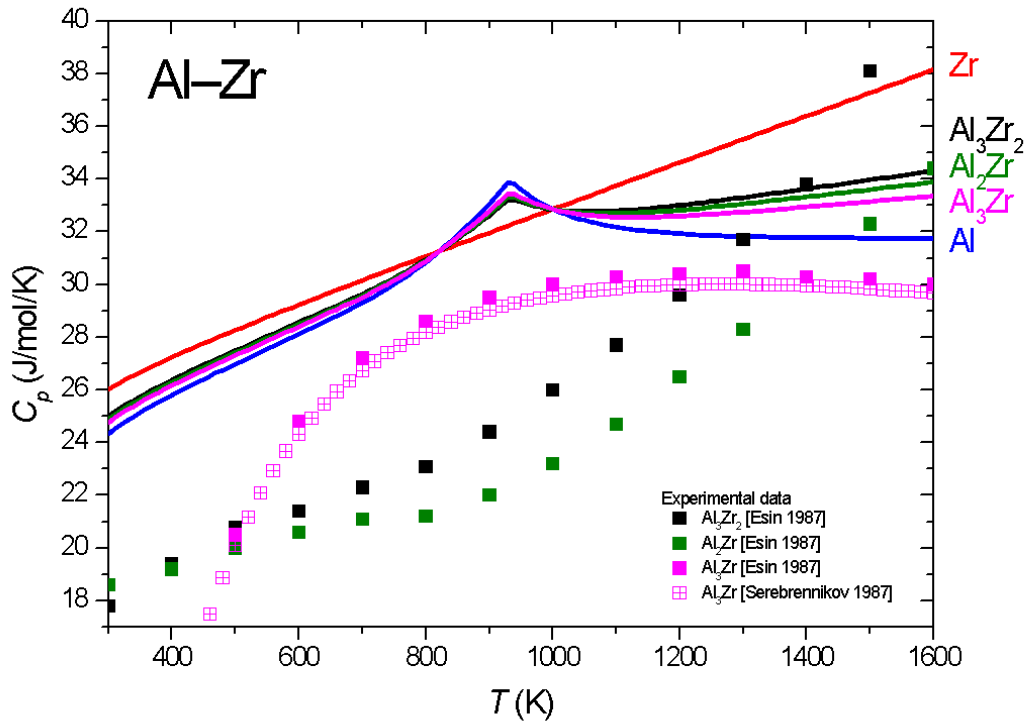


Fig. 6. Experimental and calculated (NKR, lines)  $C_p$  data in Al–Zr system. Pure elements from the SGTE Unary database are shown for comparison. Same colors are used for points and curves.

## 4. Discussion

### 4.1. $C_p$ depression

As already mentioned, most often the measured  $C_p$  is lower than expected from the NKR. In Fig. 7, we plotted, at the chosen temperature of 800 K, the difference between the experimental  $C_p$  and the  $C_p$  predicted from the NKR as a function of the enthalpy of formation. Despite the large scatter, a certain correlation can be established showing that the more negative the enthalpy of formation, the larger the deviation from the NKR. This may be associated with stronger bonds and less vibrations. On the other hand, this observation may seem contradictory to the observation and prediction that excess heat capacity should increase with more negative enthalpies of mixing for solutions [49]. However, this has been established for solutions (not for compounds as in our study, and as mentioned in this paper, one should be very careful with the reference state) and for the high temperature limit (one could therefore get a change of the sign of excess heat capacity as a function of temperature).

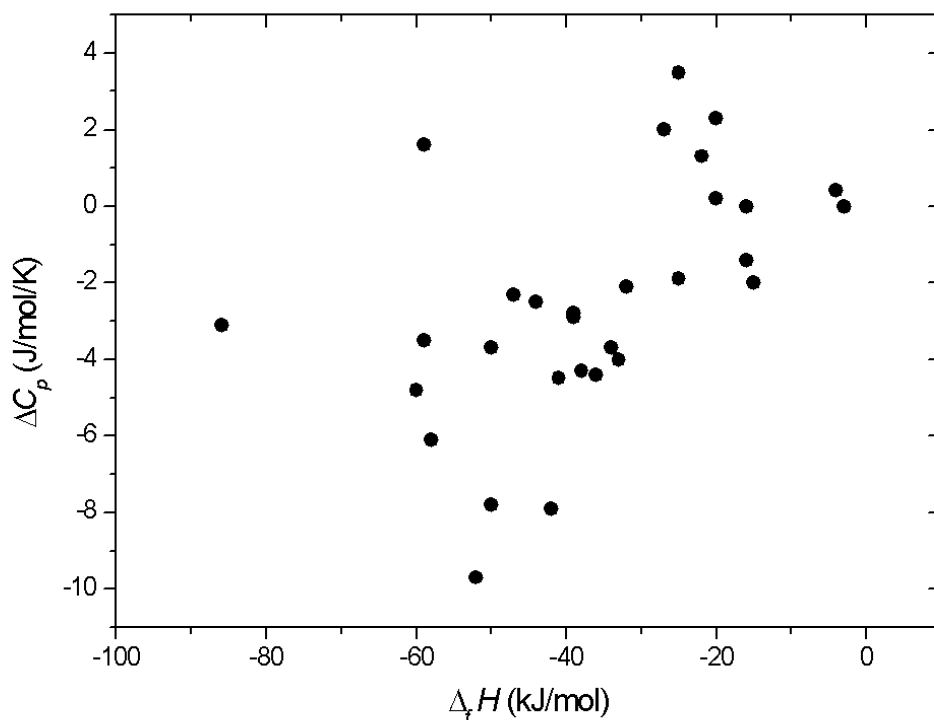


Fig. 7: Difference between observed and calculated  $C_p$  with the NKR as a function of the enthalpy of formation of the compounds (the list of compounds with numerical data and references can be found in Supplementary Materials).

#### 4.2. Reverse NKR

The reverse NKR was in principle a seducing approach. But many difficulties arose in our investigation. Some are related to the lack of good quality data to evaluate the reliability of the NKR and the way  $C_p$  changes as a function of the constituting elements and the composition. In our systematic scan of the literature, we could find experimental data in only 24 binary Al–X systems. In the systems in which measurements exist, it is rare that all the compounds have been measured. For a given compound, it happens frequently that the  $C_p$  is known only at a single temperature or as an average  $C_p$  deduced from a single measurement of the heat content. When heat content measurements are available at different temperatures, they cannot give much more than a fitted linear  $C_p$  as a function of temperature. This is not sufficient for the evaluation of the NKR for which direct and accurate  $C_p$  measurement is necessary.

For the systems in which data does exist, there are frequent interferences with phenomena having effect on the  $C_p$  like order-disorder transitions, magnetic transitions or polymorphism (with a related enthalpy of transformation). Even in the absence of order-disorder transition, site mixing exists for the non-stoichiometric compounds even at the stoichiometric composition and this also contributes to the  $C_p$ .

For the reverse approach, not all the systems are useful to perform the extrapolation, because the  $C_p$  of the second element should be perfectly defined. This excludes, in principle, X

elements like gases (H, N, O), elements with melting points similar to or lower than that of Al (As, P, Sb, Sn), elements with allotropic transformation (Fe, Mn, Co) or with magnetic order (Fe, Co, Ni) inducing anomalies on the  $C_p$ .

There is therefore a real need for measurements of compounds that have never been measured, especially those rich in aluminum and in systems involving a high melting point element. Measurements in systems such as Al–Hf, Al–Mo, Al–Re, Al–Ru, Al–Ta, Al–W would be particularly useful.

Also, measurements in the *fcc* solid solution based on aluminum would be highly desirable. Measurements for different compositions would be very interesting to understand how  $C_p$  continually changes as a function of the composition in the solid solution. However, only a few elements have a large solubility in Al (Ag, Mg, Zn...). Unfortunately, none of them induces a positive slope of the solidus that would make the *fcc* phase stable above the melting point of pure Al. This is encountered often on the other side of the phase diagram when the *X* element is *fcc* and Al has a large solubility (Ag, Au, Cu, Ir, Ni, Pd...). The possibility to have ordered *fcc* phases in the phase diagram could also be considered.

From the analysis of the data we could collect, it appears that the NKR results in a poor description of the  $C_p$  below the melting point of Al. This is also the case at room temperature, contrary to the current belief that NKR is a good approximation at low temperature and gets worse at higher temperature [10, 50]. In most cases, too high values are calculated. Not even the trends as a function of composition can be reproduced: for Al–Ni and Al–Fe, the NKR does not predict any change while a systematic increase (in the case of Al–Ni) or decrease (in the case of Al–Fe) of  $C_p$  is observed as a function of Al composition. For Al–Cu, an opposite trend to what is observed experimentally is observed. Additional discrepancies are also encountered when magnetic or structural disordering occurs in the compounds which can evidently not be taken into account within the NKR.

One thing that is conveniently reproduced by the NKR, as far as can be judged from the data available, is the slope of the  $C_p$  *i.e.*  $\frac{\partial C_p}{\partial T}$ .

The accuracy of the NKR is therefore not sufficient enough to allow usage of the reverse approach to derive the  $C_p$  of Al above its melting point. As an example, the calculated  $C_p$  of Al by the reverse NKR is shown in Fig. 8 using the experimental  $C_p$  of different compounds in the Al–Zr system. Not only are the results very different when different compounds are considered but also the calculated  $C_p$  for pure Al from the reverse NKR is very low in any case.

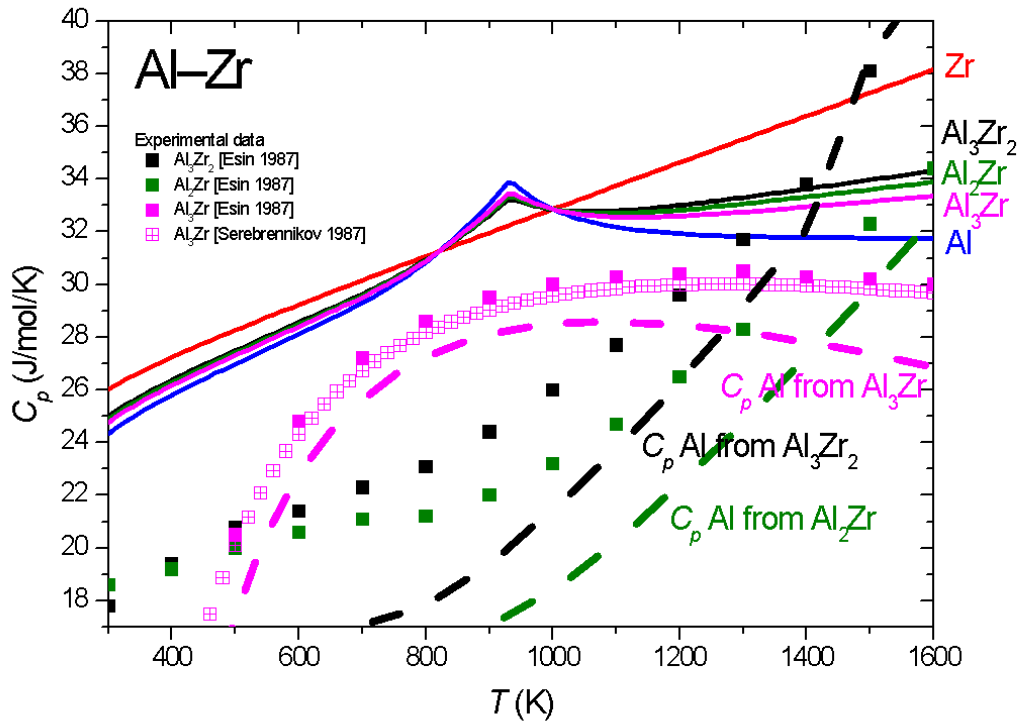


Fig. 8. Calculated  $C_p$  of fcc Al using the reverse NKR (dashed lines) and the experimental data of three different compounds in the Al–Zr system. Same colors are used for points and curves.

Extending to other than Al-based systems, it seems that there is a need for the validation of the NKR. It appears that there are no systematic studies showing how reliable it is, even in ranges where the  $C_p$  of both components are clearly defined. There exists validation on oxides [50, 51], borides [4] and solutions of compounds (*e.g.* between InP and InAs or between GaAs and InAs [52]) and quite limited comparisons for intermetallic compounds [6, 53], but as far as we are aware there is no systematic comparison of the experimental data with the NKR for intermetallic compounds. For oxides an accuracy of about 3 % is stated [50, 51] but note that this is for the  $C_p$  of ternary oxides calculated from the  $C_p$  of the binary ones *i.e.* significantly different from what we are investigating (compounds from the pure elements). Schick *et al.* mention a general accuracy of 15 % [4]. Kauwe *et al.* [10] made a systematic comparison for 263 compounds and obtained a 14 % error but the comparison is made with JANAF tables rather than with original experimental data. The list of compounds is not known but probably contains few intermetallic compounds. It is remarkable that such a widely used approximation has not been better validated, in particular for intermetallic systems. 15 % error is about what we obtain in our systematic evaluation, but, for the first time, we could detect deviations that are systematic (a too high calculated  $C_p$ ). As far as we know such a systematic deviation has never been mentioned.

#### 4.3. What are the consequences of an incorrect evaluation of the $C_p$ of a compound in a system?

In order to evaluate the consequences of an incorrect  $C_p$  estimation, we performed a thermodynamic assessment of a simple system using different models for the  $C_p$ . To avoid the

difficulties posed by Al, we have chosen a system for which the application of the NKR does not pose any problem *a priori*: the Cr–Nb system. A thermodynamic assessment of this system was published in Ref. [54]. We basically used the same data as in this reference but did not consider the non-stoichiometry of the intermetallic compound.

In a first assessment, the NKR was used (as in Ref. [54]). In a second assessment, a deviation of  $-2$  J/mol/K for the  $C_p$  was used. This choice was motivated by the fact that it is the order of magnitude of the differences observed above in many Al-based systems and because this value allows to better match the reported  $C_p$  values calculated in this system [55]. The effects of the change of the  $C_p$  can be evaluated on the resulting phase diagram, enthalpies, and entropies of formation of the intermetallic phase in Figs. 9-13. In the absence of high temperature calorimetric data for the enthalpy of formation of the compound, the optimization was constrained to the low temperature enthalpy of formation calculated by DFT. A very similar reproduction of the phase diagram data is obtained with the two models. However, constant enthalpy and entropy of formation are only observed when the NKR is fulfilled as explained in Section 2 and seen from Eqs. 1-3. The deviation from the NKR gives extra  $T$  dependent terms in the Gibbs energy which makes the enthalpy and entropy of formation no longer constant with temperature. The change for the enthalpy between 0 K and the temperature of melting is approximately  $-4$  kJ/mol.

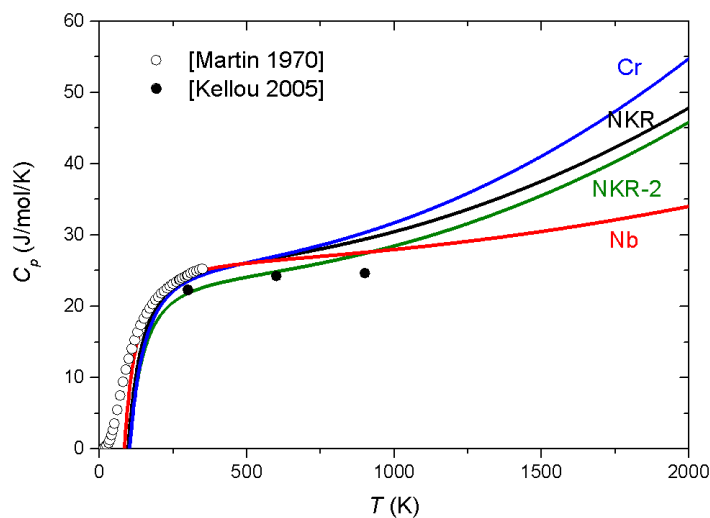


Fig. 9.  $C_p$  of pure Cr and Nb, calculated  $C_p$  of  $Cr_2Nb$  using the two models investigated (NKR and a corrected NKR with an offset of  $-2$  J/mol/K), experimental [56] and calculated [55] data.

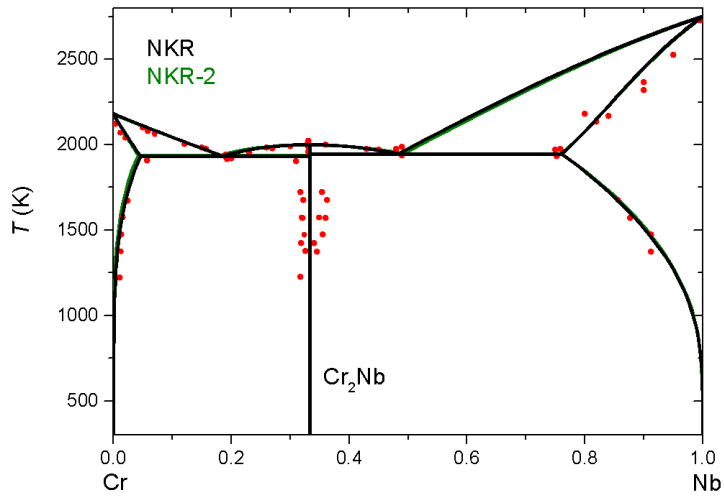


Fig. 10. Optimized Cr–Nb system with the two models NKR and NKR-2. Experimental data are also shown (for a complete description see Ref. [54]).

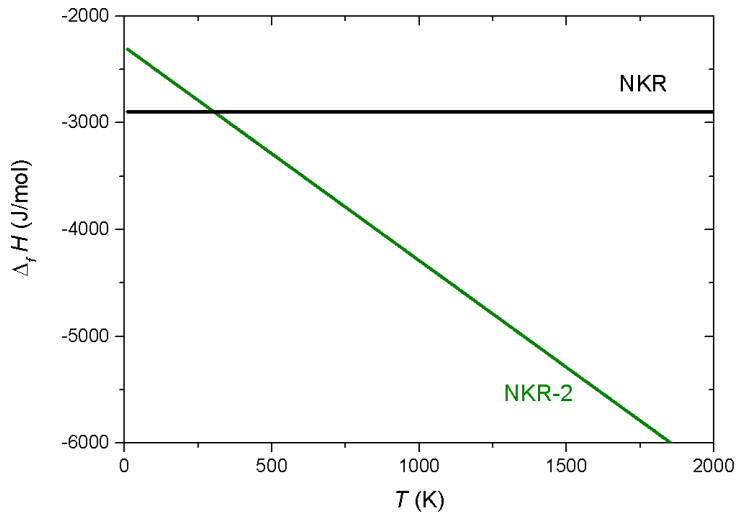


Fig. 11. Calculated enthalpy of formation of  $Cr_2Nb$  with the two models NKR and NKR-2.



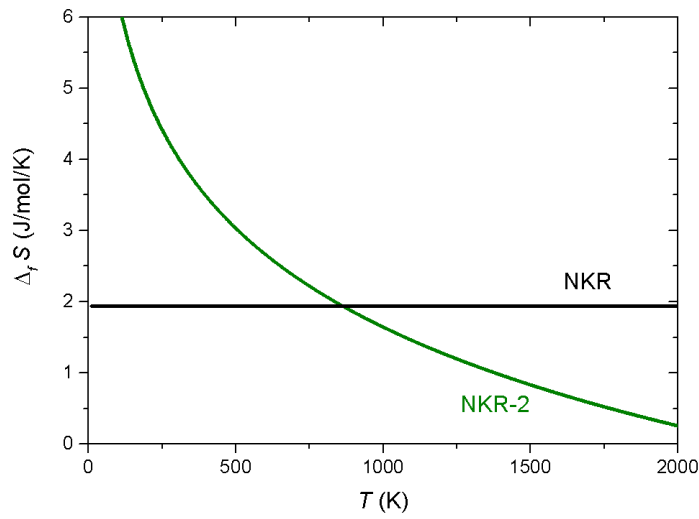


Fig. 12. Calculated entropy of formation of  $\text{Cr}_2\text{Nb}$  with the two models NKR and NKR-2.

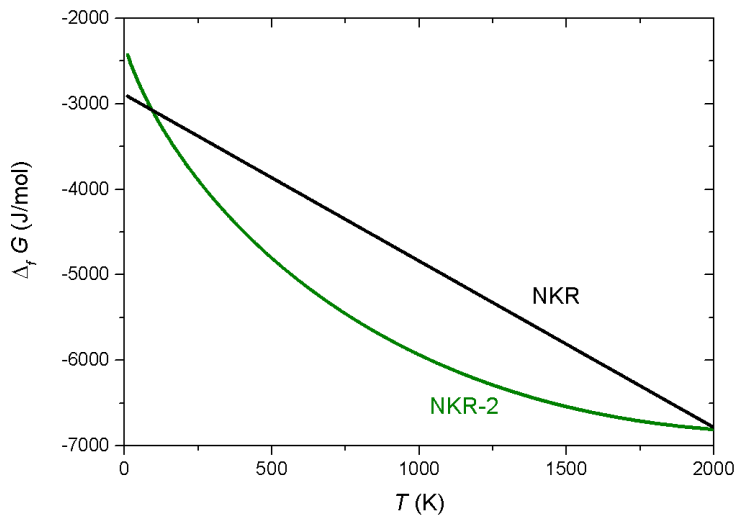


Fig. 13. Calculated Gibbs energy of formation of  $\text{Cr}_2\text{Nb}$  with the two models NKR and NKR-2.

As a conclusion, we can say that, if the presence of the kink itself in the Al-based compounds may have small consequences because it is located in a small temperature range, on the contrary a systematic deviation by values such as  $-2 \text{ J/mol/K}$ , or more, of the  $C_p$  may have large consequences on the estimation of both enthalpies and entropies of formation of compounds.

#### 4.4. Other techniques to evaluate the $C_p$ of fcc Al

One option to evaluate  $C_p$  would be to use DFT calculated data for Al. This has been investigated in particular by Bigdeli *et al.* [3]. These authors then define an instability temperature above which the solid can no longer exist. The  $C_p$  is then kept constant from this temperature.

Another option, as proposed together with the development of 3<sup>rd</sup> generation descriptions of the pure elements, would be to leave the  $C_p$  increase with temperature as obtained by DFT calculation, without introducing any break point in the function describing the Gibbs energy of the pure element [57]. As discussed before, this will inevitably result in the restabilization of the *fcc* phase at high temperature. The recent introduction of the Equal Entropy Criterion, which allows to discard this undesired phase from the calculation [58], brings hope that this will no longer be a problem [57]. However, this criterion is also subject to discussion [59].

An interesting technique that could be explored includes the use of high pressure. The melting point of Al is known to increase steeply as a function of pressure. At the relatively moderate pressure of 4 GPa, the melting point reaches 1200 K [60], *i.e.* the instability temperature at which the structure is thought to collapse into the liquid phase (at ambient pressure) [3]. This procedure was suggested in Ref. [61]. and would allow to avoid the melting and get data directly for *fcc* Al at temperatures above the normal melting. The data could, of course, be corrected from the  $C_p$  change due to the pressure. This should be done with a convenient high-pressure model and/or using the comparison between the measurements and the available data at temperatures below the normal melting point. Technically, devices exist to perform such measurements up to 8 GPa [62] (for a review see *e.g.* [63]). The  $C_p$  of liquid aluminum is known at 3000 bar (0.3 GPa) [64] up to 4000 K. For the solid phase it has been measured at room temperature up to 10 GPa [65-67]. New measurements appear to be necessary to fulfill the requirements of deriving the  $C_p$  of the metastable *fcc* phase above its melting point.

#### 4.5. Other techniques to evaluate the $C_p$ of compounds

If one wants to get rid of the NKR, it is evidently possible to use a standalone equation for the description of the Gibbs energy of a compound. However, in the absence of experimental or calculated  $C_p$  data, this is almost impossible given the number of parameters it involves. The measurement of  $C_p$  is a difficult task. On the other hand, if it is quite straightforward nowadays to obtain enthalpies of formation for compounds by DFT, it is much more difficult and time consuming to obtain  $C_p$  by phonon calculations. This means that it is still very important to have access to reasonable methods for estimating the  $C_p$ .

The method pointed out by Kubaschewski and Alcock [68] consisting in considering a constant  $C_p$  equal to  $\sim 26$  J/mol/K at room temperature and a constant  $C_p$  equal to  $\sim 30$  J/mol/K at the compound melting point is actually not worse than NKR for the systems we present here.

In order to suppress the kink associated with the presence of aluminum when one uses the NKR, it was recently proposed by Shick *et al.* [4] to fit the NKR in the region far from the kink. From the melting temperature of the compound, the  $C_p$  is then kept fixed. If this approach is able to suppress the kink, it still suffers from the remaining weaknesses of the NKR.

There are several reports of using machine learning to predict  $C_p$  [10, 69-71]. Note that, as far as the evaluation of the  $C_p$  of compounds is concerned, machine learning is so far not resulting in better estimates than the NKR [10].

## 5. A modified NKR

Another approach is proposed in the following which allows to keep the flexibility and universality of the NKR while avoiding the spurious kink present in aluminum compounds.

If the anomaly observed in pure *fcc* Al showing a sudden rise of the  $C_p$  before melting is related to a so-called pre-melting with a sudden increase of quasi-harmonicity, electronic heat capacity and thermal vacancy contributions, then there is obviously no reason to keep it in the calculation of other compounds or solutions that melt at a different temperature. Instead, this increase could be (or should be?) displaced to the actual melting of the compound. This phenomenon is illustrated by the comparison between Figs. S2 and S3 in the Supplementary Materials showing that the respective  $C_p$  of the pure elements rationalize much better when plotted as a function of the temperature relative to the melting temperature of each element rather than to the temperature itself. Note the strange behavior of Yb  $C_p$  indicating a probable error in the SGTE Unary database.

In the present model, the same rule of mixing of the  $C_p$  as in the NKR is applied but, instead of taking the  $C_p$  as an average of the  $C_p$  of the pure elements at the same temperature (Eq. 1), we normalize the different temperatures to the melting point of the pure elements and the compounds and evaluate  $C_p$  at that temperature for each element. This is illustrated in Fig. 14 and is expressed as:

$$T_i' = T \frac{T_m^i}{T_m^{compd}} \quad (4)$$

$$C_p^{Ax_A Bx_B}(T) = x_A C_p^A(T_A') + x_B C_p^B(T_B') \quad (5)$$

This makes the  $C_p$  of the compound at its melting temperature  $T_m^{compd}$  equal to the composition average of the  $C_p$  of the two pure elements at their respective melting temperatures.

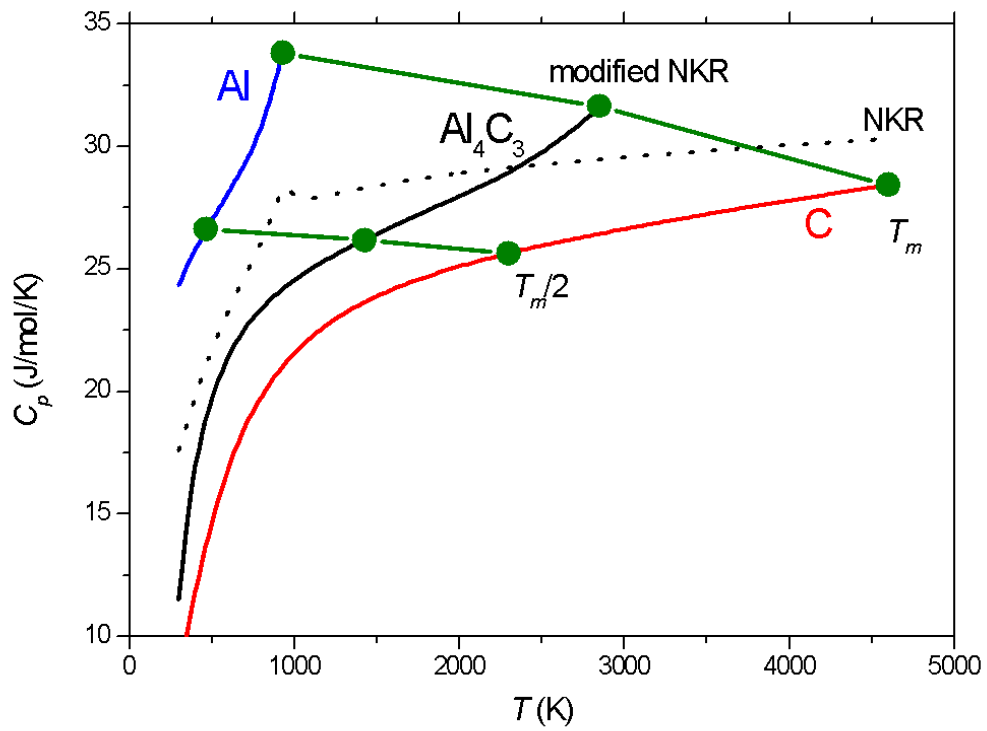


Fig. 14. Modified NKR (solid line) compared to the normal NKR (dotted line) illustrated with the example of  $Al_4C_3$ .

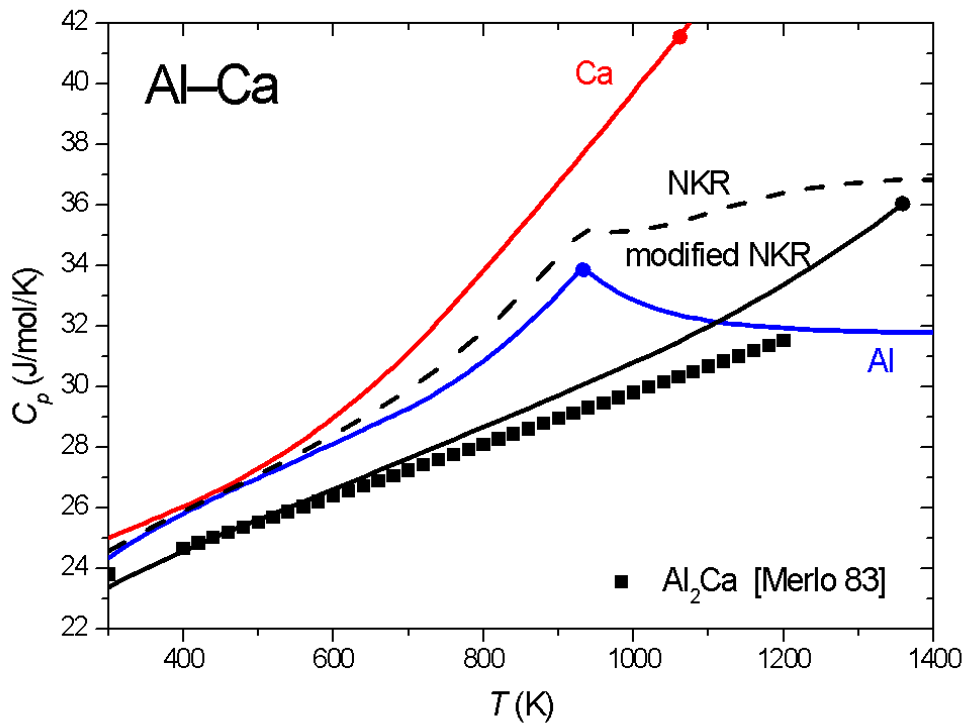


Fig. 15. Modified NKR approach (solid line) applied to  $\text{Al}_2\text{Ca}$  in Al-Ca system compared with the normal NKR (dashed line). The pure elements are indicated for comparison. The circle points indicate the melting points of the pure elements and of the compound.

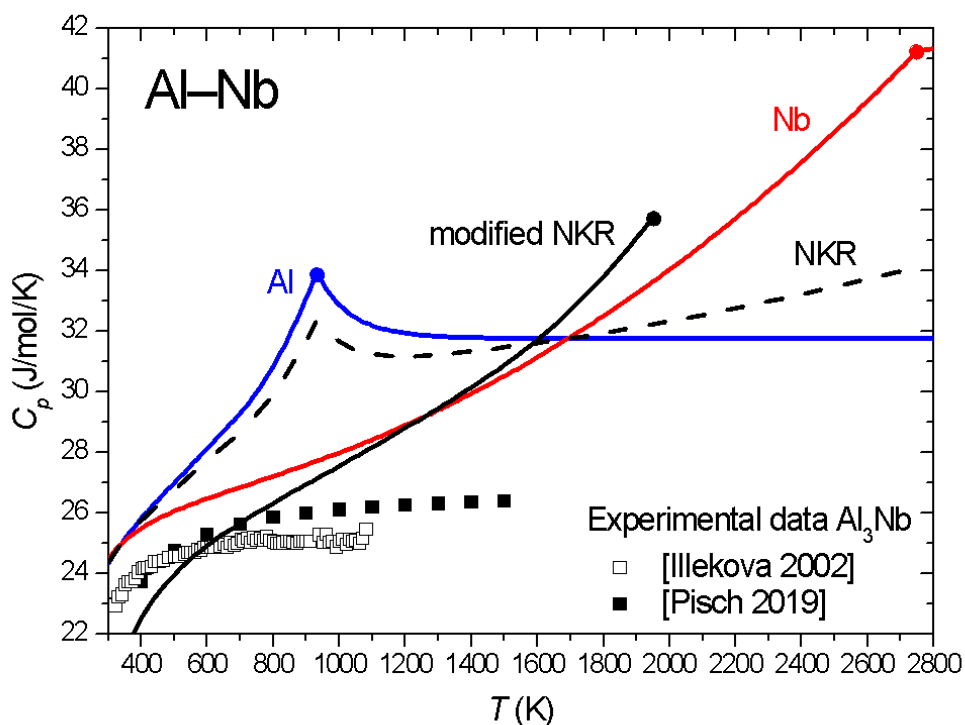


Fig. 16. Modified NKR approach (solid line) applied to  $\text{Al}_3\text{Nb}$  in Al–Nb system compared with the normal NKR (dashed line). The pure elements are indicated for comparison. The circle points indicate the melting points of the pure elements and of the compound.

The results can be seen for a couple of systems in Figs. 15 and 16 and in Supplementary Materials for all the systems.

The improvement compared to NKR is significant and is mainly due to the fact that the calculated  $C_p$  is lower because the rise of the  $C_p$  is displaced to the melting temperature of the compound. The new model remains an estimation and, in some systems, the agreement with experimental data is only relative (see *e.g.* the temperature dependence for  $\text{Al}_3\text{Nb}$  in Fig. 16) emphasizing the need to use preferentially the experimental data in thermodynamic assessments when available.

An important consequence and great advantage of the use of this model is that we no longer need a definition of *fcc* Al above its melting point (at least as shown here for compounds), which is still a matter of controversy, because there is no need to define the compounds above their melting points.

From the calculation point of view, and before this function is implemented in thermodynamic calculation software, it is possible to calculate the different coefficients required to define the Gibbs energy using an Excel calculation sheet, such as the one provided as Supplementary Material to this article.

It is also suggested that the same model could be applied to phases with an order-disorder transition (see *e.g.* different phases in Al–Fe system), replacing the melting temperature by the

order-disorder transition temperature. This would allow one to reproduce the kink observed experimentally on the  $C_p$  curve.

The proposed model can evidently be applied not only to Al systems but to any kind of systems. Furthermore, it is not limited to binary compounds.

Two difficulties are still encountered. Like in the approach of Schick *et al.* [4], one needs to estimate the melting temperature of the compound, which needs to be known or estimated in the model. In a thermodynamic assessment, as this value is not set *a priori*, then an estimate should be used because it needs to be used as input for the model. This does not seem to be a major difficulty because a chosen melting temperature above the final melting point will work adequately as well. For compounds that do not melt congruently (peritectic...), an estimate of the metastable melting should be done.

It is important to note that the approach presented here may be useful for compounds and the definition of the related end-members but not for the substitutional or interstitial solutions based on aluminum whose reference term should always be defined using the GHSERAL, since it must be able to extrapolate to pure aluminum. This will always cause problems for the *fcc* solid solutions with aluminum not only on the aluminum rich side but also on the *X* rich side if *X* is *fcc* (in this regard Al–Ni system is particularly interesting because the disordered *fcc* solid solution based on aluminum extends quite a lot and additionally there is the ordered  $L1_2$  phase). This is also a problem for ordered phases that need a disordered contribution based on the classical solution model. In an upcoming paper, we will address the case of solutions. The question of solutions between compounds described with our method should also be addressed.

Finally, this approach seems to be more easily adaptable to the classical 2<sup>nd</sup> generation system description than to the new 3<sup>rd</sup> generation description of the elements. The adaptation to 3<sup>rd</sup> generation descriptions most likely necessitates more work.

## 6. Conclusions

From a systematic investigation of the reported  $C_p$  measurements of Al-based compounds in the literature, we could evaluate the accuracy of the NKR in these systems. This is the first time that such an evaluation is conducted for metallic systems. We have shown that deviations of more than 2 J/mol/K are frequently observed, and that this deviation may cause a significant difference in estimated enthalpies and entropies of formation when a thermodynamic assessment is carried out. The NKR approximation does not even manage to qualitatively reproduce the trends observed as a function of composition in the different systems studied. It was therefore found to not be accurate enough to be used in a reverse manner in order to get an estimate of the  $C_p$  of *fcc* Al above its melting point, which was the initial purpose of this paper. Indeed, the errors made by this approximation are much larger than the errors introduced by the kink related to the  $C_p$  of *fcc* aluminum occurring around its melting temperature. Therefore, a good practice is to use  $C_p$  data, if available, to optimize the Gibbs energy of each phase and, if not, to either measure or calculate the  $C_p$  of the different compounds before attempting a thermodynamic assessment. NKR or other approximation should only be used where data is not available. We nevertheless proposed a new approach allowing one to get rid of the kink. The new approach is found to give a much better estimate of the  $C_p$  than the conventional NKR. It also offers the great advantage to avoid the need of a definition of *fcc* Al above its melting temperature. This proposal needs to be further evaluated.

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## Data availability statement

The raw data required to reproduce these findings are available to download as a Supplementary Material to this publication. The processed data required to reproduce these findings are available to download as a Supplementary Material to this publication.

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