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LETTER TO THE EDITOR

Estimates of configurational interactions in binary alloys from diffuse scattering data

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Abstract. Previously described cluster methods are used to estimate pairwise configurational interactions $V(r)$ in a number of binary alloys from data on the diffuse scattering of neutrons or x-rays by these alloys. The temperature dependence of the parameters V estimated from the most reliable (neutron) data appears to be rather weak. The concentration dependence for the Ni–Cu alloys studied is, in contrast, strong and unusual; this seems to be due to band-structure effects. First-principles estimates of V obtained using the coherent-potential approximation agree in order of magnitude with our V while those based on the Connolly and Williams approach, neglecting non-nearest-neighbour interactions, seem to overestimate the values of V considerably.

The development of microscopic methods for calculating the phase diagrams and stability of alloys is known to be a problem in metal physics. In the statistical theory of alloys such methods are formulated in terms of configurational Hamiltonians, including effective n -site interactions $V^{(n)}(r_1, r_2, \dots, r_n)$ as the main parameters of the theory; see, e.g., Khachaturian (1974), Gonis *et al* (1987). Recently several theoretical approaches for calculating $V^{(n)}$ have been suggested (see Connolly and Williams (1983), Gonis *et al* (1987), and references therein) and a number of calculations have been performed (Terakura *et al* 1987, Wei *et al* 1987, Carlsson and Sanchez 1988). However, estimates of $V^{(n)}$ obtained by different methods sometimes disagree by more than an order of magnitude (see below), so quantitative estimates of $V^{(n)}$ obtained from experiments seem to be highly desirable.

Early estimates were made by Clapp and Moss (1966, 1968). They used data on the short-range-order (SRO) parameters $\alpha(r_i) = \alpha_i$, or their Fourier components $\alpha(\mathbf{k})$ (which are proportional to the intensity of the diffuse scattering with momentum transfer \mathbf{k}), and interpreted these using the high-temperature approximation for $\alpha(\mathbf{k})$ suggested earlier by Krivoglaz (1957, 1984). However, the Krivoglaz–Clapp and Moss (KCM) formula corresponds to the mean-field approximation for $\alpha(\mathbf{k})$ and can be justified only if the interactions V are much less than the temperature T . In real alloys values of V/T are often not small and can even be large, and reliance cannot be placed on estimates obtained using the KCM expression.

It has been suggested that the variational cluster field method (CFM) may be of use in calculating statistical properties of alloys with strong interactions $V \gtrsim T$, (see Vaks *et al* (1988), to be referred to as I, and references therein). The CFM is a simplified version of the cluster variation method (Kikuchi 1951, Sanchez *et al* 1984) in which long-ranged

interactions characteristic of real alloys can also readily be taken into account. The results in the CFM can be written in the form of 'cluster-cumulant' expansions in terms of the contributions of n -particle correlations, with increasing n . It was shown in I that these expansions converge rapidly at values of V characteristic of substitutional alloys. Values for pair interactions $V^{(2)}$ in the alloy $\text{Ni}_{0.765}\text{Fe}_{0.235}$ were also estimated in I from the SRO data of Lefebvre *et al* (1981).

In this Letter we apply the CFM to estimate the interactions V in a number of other substitutional alloys, A_{1-x}B_x , for which SRO parameter data are available. As in I, we include in the analysis only pair interactions $V^{(2)}(r_i) = V_i$ (which can be understood as 'mixing potentials' $V(r_i) = V_i^{\text{AA}} + V_i^{\text{BB}} - 2V_i^{\text{AB}}$) and neglect many-site $V^{(n)}$ interactions as well as terms involving derivatives with respect to concentration: $\partial V_i/\partial X$, $\partial^2 V_i/\partial X^2$ (see I). Making these approximations is not essential to the method, but we have made them since only pair parameters α_i are determined in the diffuse scattering. Thus to make the 'inverse' problem of estimating V from α_i well defined we must restrict the number of unknown $V^{(n)}$ by using $V^{(2)} = V_i$. Below we show that the non-pairwise $V^{(n)}$ can also be estimated if we use some additional experimental information, e.g. that on the phase diagram. In the example considered below, including $V^{(n)} = V^{(3)}$ has a relatively small effect on values of V_i . Thus errors in our estimates of V_i due to neglecting $V^{(n)}$, $\partial V_i/\partial X$ and $\partial^2 V_i/\partial X^2$ are apparently not large.

Analysis of the available data on the diffuse scattering of neutrons or x-rays by single-crystal disordered alloys shows that quantitative information on V_i is at present obtained mainly from neutron scattering data, such as those given by Vrijen and Radelaer (1978) for $\text{Ni}_{1-x}\text{Cu}_x$, Lefebvre *et al* (1981) for Ni_3Fe and Schweika (1985) for $\text{Ni}_{89}\text{Cr}_{11}$. The accuracy of the determination of α_i in the x-ray experiments (e.g. by Chen *et al* (1979) for Cu_3Au , Metcalfe and Leake (1975) for CuAu and Epperson *et al* (1978) for $\text{Cu}_{1-x}\text{Al}_x$) seems to be much lower. This is indicated by both significant violations of the normalising conditions $\alpha_0 = 1$ in these data and sharp variations of α_i and the corresponding V_i with temperature or concentration (see table 1).

As was discussed in I, and earlier by Krivoglaz (1957, 1984), the most convenient form for microscopic analysis of the SRO data is that for the quantity $\alpha^{-1}(\mathbf{k})$:

$$\frac{1}{\alpha(\mathbf{k})} = \sum_i a_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) \quad (1)$$

where the sum is taken over all crystal lattice vectors \mathbf{r}_i . Unfortunately, in most of the experimental work only Cowley-Warren parameters α_i are presented. Since the α_i (unlike the a_i in (1)) decrease very slowly with the increase of r_i , a great number of α_i are needed to describe the data, and values of α_i with large r_i usually have low accuracy. Because of this, we applied an iterative procedure to estimate a_i from the experimental α_i . This algorithm is stable and rapidly convergent for 'good', intrinsically consistent neutron data but is not so good for the less accurate α_i obtained from the x-ray experiments. Therefore, estimates for the alloys Ni-Fe, Ni-Cr and Ni-Cu in table 1 are much more reliable than those for Cu-Au and Cu-Al.

With the known a_i , values of V_i were found by the method described in I for the alloy Ni_3Fe . We used the most accurate ' δ -approximation' including about 30 different types of cluster—in particular, six-site ones. The convergence of the cluster-cumulant expansion used was usually as rapid as in the case discussed in I.

The estimates obtained for the V_i are presented in table 1 and in figure 1. It is firstly seen that for the 'reliable' data (for Ni_3Fe and Ni-Cu alloys) the variation of the main

Table 1. Pairwise configurational potentials $V_i = V(r_i)$ (in K) in the disordered FCC alloys $A_{1-x}B_x$. The sources of the SRO data are given as footnotes.

Alloy A-B	x	T (K)	$2r_i/a$ $\alpha_{0,exp}$	110	200	211	220	310	222	321	400	330	$V_{NN}^{(3)}$
				V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9	
Neutron scattering													
Ni-Fe ^a	0.235	745	1.03	711	-205	49	16	-25	-26	1	-21	-8	—
		780	1.02	663	-238	42	27	-22	-19	15	-9	8	—
		808	0.93	690	-254	25	9	6	-27	14	-3	14	—
		958	0.99	717	-159	66	47	-12	8	5	19	-8	—
		780	1.02	797	-225	45	29	-22	-19	15	-9	8	-250
Ni-Cr ^b	0.11	833	0.998	617	-243	-34	114	2	3	-24	26	-60	—
Ni-Cu ^c	0.2	723	1	-287	239	-58	17	4	22	7	9	4	—
		873	1	-292	262	-75	67	-4	34	0	14	0	—
	0.435	723	1	-267	165	-19	51	-47	101	-18	147	-24	—
		873	1	-277	151	-3	8	-32	47	-6	212	-21	—
	0.6	723	1	-353	497	-103	219	-56	115	-24	70	-16	—
		873	1	-400	621	-139	268	-65	144	-30	91	-17	—
	0.7	723	1	-456	770	-182	446	-118	257	-64	162	-44	—
		873	1	-371	531	-101	257	-67	121	-30	76	-23	—
X-ray scattering													
Cu-Au ^d	0.25	693	1.29	267	-114	-56	-5	142	-16	29	-19	20	—
		748	1.38	554	-47	-39	-8	100	-47	1	92	25	—
Cu-Au ^e	0.5	700	1.26	568	-192	-36	-95	-104	62	5	-15	-4	—
		800	1.4	374	-155	49	57	-10	17	14	-25	2	—
Cu-Al ^f	0.09	423	0.91	5000	76	247	224	78	19	-1	28	-12	—
		0.136	423	1.04	1000	329	453	306	350	210	161	202	87

^a Lefebvre *et al* (1981).^b Schweika (1985).^c Vrijen and Radelaer (1978).^d Chen *et al* (1979).^e Metcalfe and Leake (1975).^f Epperson *et al* (1978).

constants V_1 and V_2 with T is usually small. This seems natural, since the dependence on T of V_i can, generally, arise only from small effects, such as the thermal expansion, the thermal smearing of the Fermi surface and so on. The constant V_2 in Ni_3Fe changes significantly between $T = 958$ K and $T = 808$ K, but it can be connected with ferromagnetic ordering at $T = 823$ K. It is also seen that the small V_i with $i \geq 4$ as well as the V_i estimated from the x-ray data often vary significantly with T . This seems to reflect mainly the larger experimental errors for these particular V_i . Therefore, values of V_i for the alloys Cu-Au and Cu-Al in table 1 should be regarded only as order-of-magnitude estimates while the estimates for the systems Ni-Fe, Ni-Cr and Ni-Cu can be treated as quantitative.

The values of V_1 and V_2 for Ni_3Fe and $Ni_{89}Cr_{11}$ given in table 1 are similar, which apparently corresponds to the similarity of the Fe and Cr properties. It is also seen that the values of V_i in the ordering alloys Ni-Fe, Ni-Cr and Cu-Au differ qualitatively from those for the decaying Ni-Cu alloys.

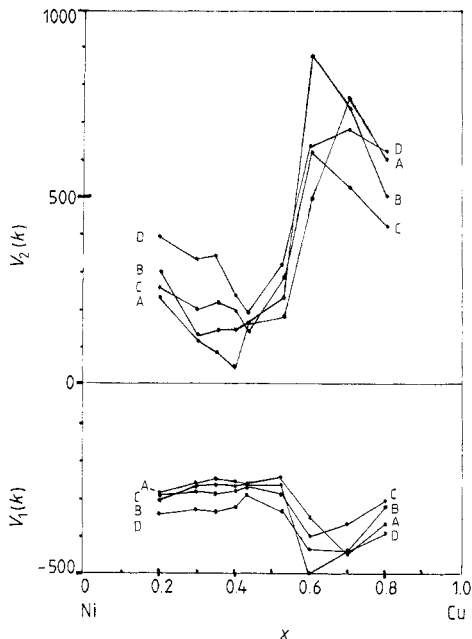


Figure 1. The concentration dependence of the interaction constants V_1 and V_2 in the alloys $\text{Ni}_{1-x}\text{Cu}_x$ at different temperatures T . Curves A, B, C and D correspond to $T = 723, 773, 873$ and 973 K, respectively.

The concentration dependence of α_i was carefully investigated by Vrijen and Radelauer (1978) for Ni–Cu alloys. The corresponding $V_i(x)$ are displayed in figure 1 and in table 1. The prominent feature of the results is a sharp variation of $V_i(x)$ for $x \approx 0.5-0.6$ while for other values of x the dependence on x is weak or moderate. These results confirm qualitatively recent first-principles estimates given by Gonis *et al* (1987), who found similar sharp variations in the V_i with the position of the Fermi level for the model of the alloy Pd–V. The concentrational anomaly in figure 1 correlates with the change in the character of the band structure of the alloys $\text{Ni}_{1-x}\text{Cu}_x$ for $x \sim x_c \approx 0.6$ discussed by Stocks *et al* (1971) and Gordon *et al* (1981): for $x > x_c$ the Fermi level leaves the d band. Thus the anomaly found in the $V_i(x)$ dependence seems to be one more manifestation of the strong band-structure effects in the lattice properties discussed by a number of authors, e.g. De Camargo *et al* (1987) and Vaks and Trefilov (1988). A search for similar anomalies in $\alpha_i(x)$ and $V_i(x)$ in other systems with band-structure anomalies (for example, in the alloys $\text{Li}_{1-x}\text{Mg}_x$ near $x_c = 0.19$ (Vaks and Trefilov 1988), $\text{Ag}_{1-x}\text{Pd}_x$ or $\text{Nb}_{1-x}\text{Mo}_x$ near $x_c = 0.4$ (Stocks *et al* 1973, De Camargo *et al* 1987)) would probably be interesting.

The values obtained for the V_i can be used for estimation of the ordering temperatures T_c . In figure 2 we present such estimates for the alloys $\text{Ni}_{1-x}\text{Fe}_x$ near $x = 0.25$. Supposing the values of V_i in the second row of table 1 to be independent of both the ordering and concentration (curves B in figure 2), we obtain a reasonable agreement with the experiment as regards values of T_c . However, the concentration dependence of these $T_c(x)$ differs noticeably from the observed one. In this connection we tried to estimate non-pairwise interactions of nearest neighbours $V_{\text{NN}}^{(n)}$, which should be added to pair-concentration-independent V_i to describe both the experimental α_i in $\text{Ni}_{0.765}\text{Fe}_{0.235}$ and

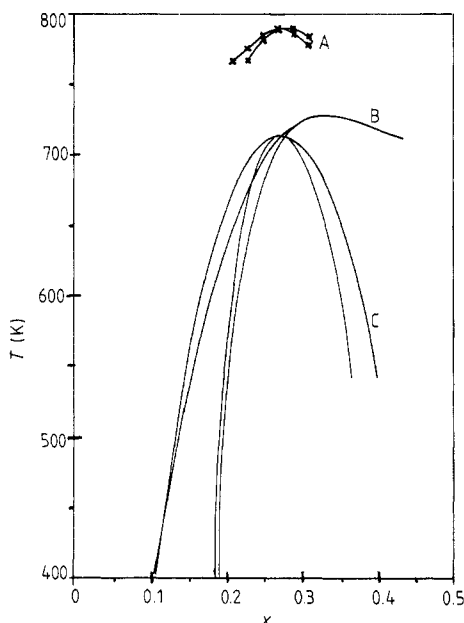


Figure 2. Temperatures $T_c(x)$ for the ordering L_{12} (of the Cu_3Au type) in the alloys $\text{Ni}_{1-x}\text{Fe}_x$. Curve A: experimental data from Van Deen and Van der Woude (1981); curve B, $T_c(x)$ calculated using interaction constants from the second row of table 1; curve C: the same with the constants from the fifth row of table 1.

the character of the concentration dependence of $T_c(x)$ near its maximum. This can be achieved at $V_{\text{NN}}^{(3)} = -250$ K and for the V_i indicated in the fifth row of table 1. The corresponding $T_c(x)$ are shown by curves C in figure 2. Effects of the four-site interaction $V_{\text{NN}}^{(4)}$ on $T_c(x)$ are much weaker than those of $V_{\text{NN}}^{(3)}$. For example, at $V_{\text{NN}}^{(3)} = 0$ we should use a much larger value $V_{\text{NN}}^{(4)} \approx 5000$ K to obtain a $T_c(x)$ similar to curves C. These estimates illustrate a possible scale of the non-pairwise potentials $V^{(n)}$ in Ni_3Fe . Comparison of the fifth and second rows of table 1 also shows that including $V^{(3)} \neq 0$ does not significantly change the estimates of pairwise V_i .

Let us now compare the values of V_i given in table 1 with their first-principles estimates. Gonis *et al* (1987) used cluster approaches based on the coherent-potential approximation and estimated the V_i for the alloy Pd-V to be $|V_1| \approx 300$ K, $|V_2| \approx 30$ K. This agrees in order of magnitude with the estimates in table 1. On the other hand, estimates using the Connolly and Williams (1983) approach seem to overestimate the values of V_1 considerably. For example, for the alloy Cu-Au Terakura *et al* (1987) found $V_1 > 10^4$ K (their v_2 is related to our V_1 by $V_1 = 4v_2$) which disagrees sharply with our estimates from the SRO data. One of the causes of the discrepancy might be the neglect in their approach of the non-nearest-neighbour interactions which, according to our estimates, are quite important for the ordering energies. For example, if we put $V_i = 0$ for all $i > 1$ in the second row of table 1 we obtain $T_c^{\text{calc}} = 310$ K, i.e. we underestimate T_c by more than twice. Thus, taking into account the non-nearest-neighbour interactions appears necessary for obtaining realistic estimates of configurational interactions in alloys.

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