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ELECTRONIC CONTRIBUTION TO THE ENTROPY OF SOLUTION*

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The nature of the entropy of solution has been studied extensively yet certain features remain unclear. One of them is its electronic nature (1) which is the main topic of this communication. The argument to be presented yields the partial (molar) entropy at infinite dilution which will, for brevity, not always be referred to by its full name. It will be shown that the variation of the entropy of carbon solution in Ni-Fe and Ni-Co alloys as a function of the Ni-Fe/Co ratio can be understood by considering the degeneracy of the screening charge.

The entropy of solution ΔS with respect to a reference entropy $\Delta S^{(o)}$ may be broken down into four components

$$\Delta S - \Delta S^{(o)} = \sum_{i=1}^4 \Delta S^{(i)}. \quad (1)$$

In this equation $\Delta S^{(1)}$ and $\Delta S^{(2)}$ denote the ionic and electronic degeneracies of the chargeless point mixture and of the charge distribution. The former may be obtained through a combinatorial (2) approach and the latter will be commented on more fully later. The sum of the contributions $\Delta S^{(3)}$ and $\Delta S^{(4)}$ denotes the excess entropy, i.e. ionic and electronic contributions to the entropy of solution stemming from property changes of the solvent. Usually, $\Delta S^{(3)}$ is termed the vibrational entropy and is rather successfully analyzed in terms of Einstein models in the long wavelength limit (2). A more realistic approach which would take into account all branches and all wave lengths of the lattice oscillations (3) as well is currently unfeasible because of the lack of data. The quantity $\Delta S^{(4)}$, finally, would involve an analysis of the influence of electronic changes due to the alloying process on the properties of the solvent. It will not be pursued here. Evidently, the separation of $\Delta S^{(3)}$ and $\Delta S^{(4)}$ is only valid to a low approximation.

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In the following, the electronic contribution $\Delta S^{(2)}$ will be discussed. It has already been noted (1) that the degeneracy of the angular momentum $m^2 = h^2 L(L+1)$ of the electron leads to an entropy

$$\Delta S^{(2)} = k \ln(2L+1). \quad (2)$$

This expression, however, is valid only for independent particles and thus not applicable to metallic solid solutions without a great deal of care. In metals, the electronic degeneracies are given by the band structure (4) and it might thus be expected that $\Delta S^{(2)}$ reflects the density of states at the Fermi level and hence the electronic specific heat, C_{el} ,

$$\Delta S^{(2)} \propto C_{el}. \quad (3)$$

This interpretation may be successful if the addition of electrons is predominant in the process of alloying (5). So far, however, little evidence is available for its support.

In the case of interstitial-transition element solid solutions neither Eq. (2) nor Eq. (3) is directly applicable since it must be expected that screening is of major importance (6). The entropy $\Delta S^{(2)}$ is then given by the degeneracy of the screening charge, as will be illustrated with Fe-Ni-C and Fe-Co-C alloys serving as an example.

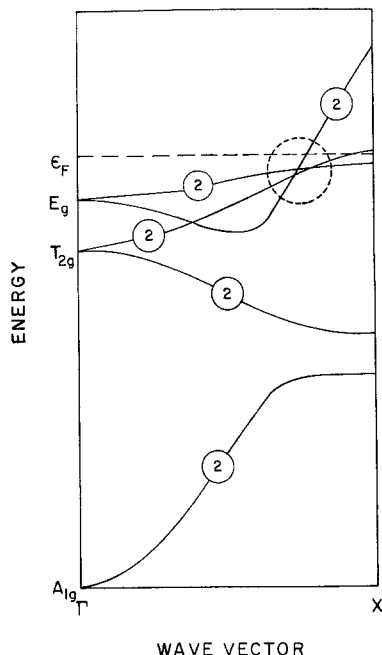


FIG. 1
Band structure of paramagnetic nickel after ref. 7. The encircled numbers give the degeneracy of the band ignoring the angular momentum.

Consider the band structure of paramagnetic nickel, a portion of which is shown in Fig. 1. This band structure is assumed to be typical of austenite. It can be seen in this figure that the Fermi level ϵ_F is located above the degeneracies encircled by the dotted line. As iron or cobalt is added to nickel, the Fermi level is expected to drop (8) and it will eventually pass through one of these degeneracies or others situated along other directions in the reciprocal lattice. It is known that this happens in the ferromagnetic state (9) and it must in principle also happen in the paramagnetic state, albeit at a different Ni/Fe or Ni/Co ratio.

Consider now the formation of a Ni-Fe/Co-C alloy. As mentioned, it must be expected that a screening charge is concentrated around the interstitial. If it is for simplicity assumed that the screening involves predominantly a redistribution of electrons at the Fermi level,

the electronic contribution to the entropy of solution will vary as the Fermi level passes through a degeneracy. If the Fermi level is located above or below the degeneracy, two energetically equal electrons (spin up and spin down) may accomplish the screening whereas four will be available at a degeneracy. Hence, it may be concluded that the contribution $\Delta S^{(2)}$ to the entropy of carbon solution resulting from the passage of the Fermi level through a degeneracy will pass through a maximum as iron or cobalt is alloyed to nickel. The height of the maximum is

$$\Delta S^{(2)} \approx k \ln 2, \quad (4)$$

if

$$\Delta S^{(0)}, \Delta S^{(1)}, \Delta S^{(3)}, \Delta S^{(4)} = \text{const.} \quad (5)$$

The experimental situation is shown in Fig. 2 and 3. It can be seen from these figures that the solid solubility of carbon in nickel-iron, and nickel-cobalt alloys as well as the partial molar entropy of carbon solution in nickel-iron alloys show extrema. The experimental extrema are broad as must be expected because in the vicinity of degeneracies the thermal energy will be comparable to the separation of the bands. The "theoretical" curve based on Eq.(4) shown in the lower portion of Fig. 3 has been drawn to reflect this thermal broadening. Its maximum was positioned according to the properties of the ferromagnetic state and, therefore, cannot be expected to coincide with the experimentally determined one.

The above argument is only qualitative, reflects a number of assumptions and is in competition with other models (1,11). In commenting on the assumptions (5) first it is noted that a dependence of either term $\Delta S^{(1)}$, $\Delta S^{(3)}$, or $\Delta S^{(4)}$ on

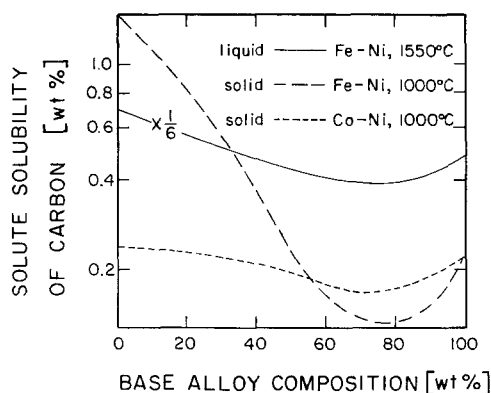


FIG. 2
Solubility of carbon in solid nickel-cobalt (10) and solid (11) and liquid (12) nickel-iron alloys

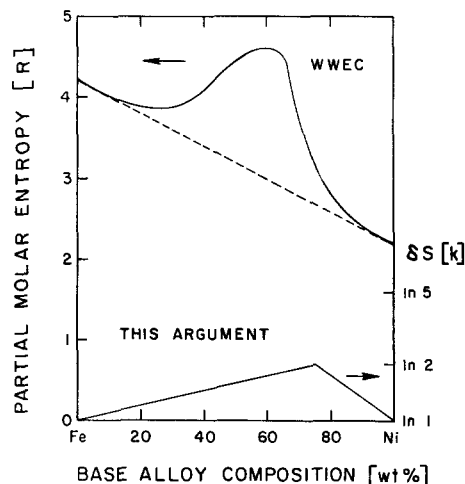


FIG. 3
Experimental (11) (WVEC) and "theoretical" (this argument) partial molar entropy of carbon solution in nickel-iron alloys

the base alloy composition can be constructed through ad hoc assumptions on the number of interstitial sites available, their mutual blocking and the variation of force constants to mention only a few. All of these assumptions will ultimately have to be justified in terms of the basic properties of the solvent and the solvent-solute interactions. The present argument does just that by singling out one contribution. The only uncertainty is the exact position and nature of the degeneracy in the paramagnetic state which, however, must be traversed by the Fermi level independently of whether a rigid band model holds or not (9). It is also for this reason that the angular degeneracy has been disregarded as it is uncertain (4) and its inclusion would not substantially alter the result.

As a final qualitative confirmation of the present argument, it is noted that the minimum of the carbon solute solubility in nickel-iron alloys persists into the liquid state as can be seen from Fig. 2. This is to be expected as all degeneracies circled in Fig. 1 are located at short wavelengths (large wave vector) and it is this portion of the dispersion curve which is left qualitatively unchanged upon melting (13).

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