METALLIC SOLID SOLUTIONS

J. FRIEDEL and A. GUINIER, Editors

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A Symposium on Their Electronic and Atomic Structure

J. Friedel and A. Guinier, *Editors*
Science Faculty of Paris, Orsay

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PREFACE

This book presents the proceedings of an International Symposium held in July 1962 at the Solid State Physics Laboratory of the Science Faculty of the University of Paris, at Orsay (France). This meeting was supported by the French Centre National de la Recherche Scientifique. Thanks are due to Professor de Gennes and Mr. Matricon, who took charge of its organization and collected the manuscripts.

The meeting dealt with the structure of metallic solid solutions. Its main object was to induce physicists dealing with both the crystallographic and the electronic aspects of that field to come together to describe and discuss their latest results and ideas.

Metallurgy is the art of preparing and using metallic alloys; for practical use, pure metals have not the requisite qualities. Considerable technical interest has evolved in the study of solid solutions that form the basis of these alloys. A vast field of study has also opened for metal physicists. One can prepare innumerable alloys not only by varying the composition of the constituent elements but also by many complex thermal treatments. Thus the theoretician has the possibility of finding a solid solution to verify one or another of his predictions.

The properties of solid solutions are so varied and often so different from those of pure metals that it soon became evident that a simple theory of an ideal solid solution could not become the basis for the entire range. The fact that they are introduced in the matrix changes the electronic structure of solute atoms. The lattice itself is no longer strictly periodic. It is influenced both by the total composition and by the distribution of the different atoms (resulting in local deformation, etc.).

The papers that are printed here are in the order of their presentation at the meeting, and fall into two parts:

1. Electronic structures: "ordinary" alloys; transitional and rare earth impurities; transitional matrices.

2. Atomic structures: local order (short-range order and Guinier-Preston zones); long-range order (classical and periodic antiphase domain boundaries).

These papers do not encompass the entire program of the meeting, nor did the program itself cover the entire field. Semimetals and heavy metals were not mentioned, and rare earth metals very little. Mechanical properties and many questions related to point defects (vacancies and interstitials) were left out also.

Emphasis was put on recent developments in the description of the electronic structure of alloys and on their direct bearing upon problems of atomic structure: prediction of atomic and magnetic interactions as well as size effects, for instance. This provided the underlying unity of the meeting. May it contribute, in a small way, to the understanding of this fascinating but complex field.

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Orsay, France
October 1963

Metallic Solid Solutions

CONTENTS

The Structure of Metallic Solid Solutions: Introductory Lecture

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Abstract. A discussion will be given of the properties of a dissolved atom, with particular reference to those properties which can be assigned to the exact many-electron wave function of the metal and those which can be defined only in terms of an approximate model. For example, as Anderson has emphasized, one can ask whether there is an uncompensated spin moment in the neighborhood of a dissolved atom or whether there is none. The concept of bound states is discussed in this connection; the writer believes there to be no exact division between the situation in which there is a bound state present and that in which there is not. In terms of models, the nature of the wave function round a dissolved atom is discussed, particularly with reference to size effects.

In looking at the properties of a metal, it is first useful to ask which of them can be assigned to the exact many-electron wave function, and which are only properties of a one-electron model. Thus we now believe that the Fermi surface can be described in terms of excitations of the exact many-electron wave function; a solid in its lowest state may have free electrons and a Fermi surface, or it may be a nonconductor. It may or may not have an antiferromagnetic superlattice. On the other hand, there is in my view never any sharp distinction, in terms of the exact wave function, between the description of electrons by localized (Wannier) wave functions and by Bloch-type wave functions.

In the same way, when we are considering dissolved metal atoms in a normal metal, we can ask whether the atom carries a magnetic moment. The moment, usually zero but, when the solute is a transition metal, often finite, is a property of the exact wave function. This moment can be

described in terms of localized wave functions[1] or nonlocalized[2] Bloch functions. This is a matter of choice. But the moment is in general non-integral. Anderson shows that, as any parameter (e.g., the sharpness of the resonance in the virtual state) is varied, the moment will vary continuously and reach zero at a fixed value of the parameter.

As far as I know, finite moments are only found on dissolved transition metals, although there is no reason in principle why this should be so. In another case one can trace theoretically the variation of the moment on an atom from an integral value to zero. Consider a hydrogen (or monovalent metal) atom approaching a metal surface. At large distances the atom will carry a moment of one Bohr magneton; when adsorbed to the surface, particularly at a kink site, it will not carry any moment at all. It would be interesting to trace theoretically the way the magnetic moment varies, with distance from the metal surface, from one Bohr magneton to zero.

The screening of impurities and the long-range fluctuation of charge are too well known for it to be necessary for me to give any review of their properties, particularly here in Paris where Professor Friedel and his school have made such important contributions to our understanding of these matters.

I would however like to make a few remarks about the bound states which appear in the one-electron model at a potential well of sufficient depth, and ask whether, in terms of *exact* many-electron wave functions, one can ask whether a bound state exists or not. A trivalent metal (Ga) dissolved in copper is an example. Can one ask whether the two 4s functions are in bound states? I think one can in terms of excited states of the whole system, such as might be investigated by the X-ray emission spectrum of the impurity. If the 4s electrons are in bound states, a peak should appear at the low-frequency end of the emission band. But states at the low-frequency end are very much broadened by Auger effect, and thus by the interaction of the electrons. So in terms of exact wave functions, the existence or otherwise of a bound state is a qualitative question only.

I would like now to look at certain consequences about the heats of solution which seem to me to follow from these considerations.

The first point that has to be emphasized about heats of solution is that they are normally small compared with the heat of formation of the constituent metals. This is shown in Table 1. The second is that heats of solution certainly show a size effect, and often become large and positive if the difference in size between solute and solvent is too big. Hume-Rothery and others[3] came to the conclusion that if the atomic radii differ by more than ca. 14%, the solubility will normally be very small, although there are of course exceptions, e.g., Zn in Cu. One has to ask, therefore, how a metal atom manages to have a size.

If both metals have the same valency, say monovalent, it is not difficult to understand this. Let us write for the wave function in the metal

Table 1

Heats of Solution of Certain Metals (*Italicized*) in Matrix (*Not Italicized*) (kcal/gram-atom)

Cu-Ag	3,480	81,800	(Cu)
Ag-Cu	2,940	69,100	(Ag)
Cu-Au	- 2,900	111,400	(Au)
Ag-Au	- 3,470		
Cu-*Zn*	- 9,180	31,500	(Zn)
Ag-*Zn*	- 1,850		
Ag-*Cd*	- 6,200	26,750	(Cd)
Au-*Cd*	- 8,500		
Ag-*Al*	- 11,900	76,100	(Al)
Au-*Sn*	- 7,000		
Cr-Ni	- 950		
Ni-Au	9,600		

$$\psi_{kW} = \psi_W(r) \exp(ikr) \tag{1}$$

where ψ_W is the solution for the lowest state, satisfying the boundary condition $\partial \psi_W / \partial r = 0$ at the boundary of an atomic cell. In the alloy, let us first suppose that both solvent and solute have the same radius r_0. Then within a sphere of radius r_0 round the solute atom A we set for the wave function $\psi_{AW'} \exp(ikr)$, where $\psi_{AW'}$ is the lowest-state wave function in the solute calculated for the value energy of the W' for which $\partial \psi_{AW'}(r)/\partial r$ vanishes at $r = r_0$. The wave function ψ_{AW} will be normalized so as to join on smoothly to the surrounding wave function; it will therefore not necessarily be normalized to unity.

If we calculate the energy from the integral

$$\int \psi^* H \psi \, dx \ldots$$

where ψ is a Slater determinant made up of these functions, then one can divide the terms that represent potential energy in this integral into (a) the interaction between charges in a polyhedron, and (b) the interaction between polyhedra. In a pure metal, owing to the high symmetry of the polyhedra, (b) is small, not more than 0.03 eV.

Thus in the alloy, if we use these wave functions, the heat of solution is zero if $\int^{r_0} |\psi_{AW'}(r)|^2 \, dt$ is unity. According as it is positive or negative, if $W' < W$, we may expect negative or positive heats of solution.

If W' < W, then a more exact solution would show some (screened) pile-up of charge on the atom for which W' < W. Huang's[4] calculation for AgAu showed that we might expect a positive energy of mixing, owing to misfit of wave function calculated for the *same* energy, and a negative energy due to this pile-up of charge. As far as I know, either may predominate.

If the atomic radii are different, a reasonable model is to take a radius r_0 at which the wave functions on both sides satisfy $\partial \psi / \partial r = 0$. Since the contributions to the energy integral inside and outside the sphere are separate, the contribution from the solute will be the same as that of an atom in its own metal, if the metal were expanded or compressed so that the atomic volume was r_0. And a similar statement can be made about the shear energy of the matrix.

This means that the energy of mixing, necessarily positive, will be given by Friedel's[5] elastic model. But the conclusion is of course subject to the assumption that normalization is maintained; if not, let us write in the alloy

$$\int_0^{r_0} |\psi_A|^2 \, dt = 1 + f$$

If one uses plane waves, ψ_A is a constant and

$$f = \left(r_0/r_1\right)^3 - 1$$

which is the result used by Blatt.[6] Calculations made in Cambridge by Munoz[7] for copper and silver give

Ag in Cu

$f = 0.17_6$ (0.26)

Cu in Ag

$f = 0.20$ (-0.24)

The figures in parentheses are obtained with Blatt's model. This transfer of charge, if W and W' are unequal will make its own contribution to the heat of mixing, which can quite easily be calculated. The results are given in Table 2. The calculated heats of mixing are rather too large, but would be lowered by the screening of the excess charge. Preliminary calculations of this, using the Thomas-Fermi method, show that the correction is about right.

Friedel[8] has also calculated the elastic terms for the mixing of one divalent metal with another, with quite good agreement with experiment.

Table 2

Contributions to Energies of Solution (eV)

	Ag in Cu	Cu in Ag
Elastic energy	0.21_5	0.17_7
Energy due to transfer of charge	0.12_1	0.13_7
Total	0.33_7	0.31_4
Observed heat of mixing	0.30	0.23

Friedel (*loc. cit.*) has used the elastic model to calculate deviations from Vegard's law, with poor success for CuAg where the elastic energy is a large part of the heat of solution, but much better success for CuZn and similar alloys. This is curious, since for Zn dissolved in Cu the negative energy of mixing must greatly outweigh the positive elastic terms. If the success of the elastic model is anything but fortuitous, the negative energy of mixing must be very insensitive to volume.

The model is of course not the only possible one; Hume-Rothery and others[9] have sought to relate the expansion in, say, copper due to the admixture of, say, 1 per cent of Zn, Ga, or Sn to the difference in valency and obtained linear plots of expansion against valency of the solute. Whether this is significant I do not know.

Turning now from the dependence of energy on volume to the energy of solution, the main problem seems to be why energies of mixing of two metals of different valency are in general so small. Take for instance Zn in Cu; the current picture involves the wave functions in zinc as being the same as in the surrounding copper atoms, but with increased amplitudes to give two electrons in the neighborhood of the zinc atom. There is no obvious reason why these wave functions should have any similarity with those in metallic zinc, which involve higher k values—although doubtless these wave functions of higher k will be present in any analysis of the screened wave functions within the zinc atomic cell into the ψ_k for metallic zinc.

Friedel[10] gave a model for estimating the heat of solution of zinc in copper or cadmium in silver, which is very successful in predicting the heat of solution. This depends essentially on the assumption that, if one substitutes a zinc *singly charged* ion for Cu^+ in the copper lattice, the energy of the conduction electrons is unaltered. If one takes this model at its face value, it would mean that Zn^+ existed in the alloy, presumably with an unbalanced spin. This is not so; CuZn does not show strong paramagnetism. The present author[11] has suggested that one might describe the state of affairs in Zn when dissolved in copper, in a way that would

incorporate both Friedel's model and the absence of paramagnetism, by denoting within the zinc atomic cell each pair of electrons with the same k-value, not by the same orbital but by a sum of products

$$\psi_k(r_1)\,\psi_B(r_2) + \psi_k(r_2)\,\psi_B(r_1)$$

where ψ_B is essentially the wave function of an electron in the Zn^+ ion. Such a model would correspond to that sometimes used for two-electron atoms; but it is not quite clear how to incorporate it in the whole Slater determinant.

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