Submitted to Journal of Physics F

LBL-2523
Preprint

A CORRELATION BETWEEN ELECTRONEGATIVITY AND ELECTRON DENSITY

Charles W. Krause and J. W. Morris, Jr.

RECEIVED
LAWRENCE
RADIATION LABORATORY

JAN 29 1974

LIBRARY AND
DOCUMENTS SECTION

December 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-2523
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

A CORRELATION BETWEEN ELECTRONEGATIVITY AND ELECTRON DENSITY

Charles W. Krause and J. W. Morris, Jr.

Department of Materials Science and Engineering,
University of California and Center for the Design of Alloys,
Inorganic Materials Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

ABSTRACT

A simple correlation between the electronegativities of Pauling and the density of outer, bonding electrons is presented. The correlation indicates some features that are required of theories of the electronic structure of alloys.

Knowledge of the distribution of bonding electron charge in a metallic alloy is necessary for the understanding of the properties of the alloy at a microscopic level. The determination of this distribution is a difficult theoretical or experimental problem because a large number of factors, which are only qualitatively understood, enter into any calculation or attempt at organizing the known data with empirical rules. One of the factors (Hume-Rothery 1967, Barrett and Massalski 1966) that enters into the study of the charge distribution in alloys is the electrochemical effect which, in the case of binary alloys, is the transfer of electronic charge from atoms of one species to the atoms of the other species. To each element is assigned a value for the electronegativity, which is the ability of an atom of that element in an alloy to attract extra bonding charge to itself, and the amount of charge transferred is assumed to be determined by the difference in electronegativities of the two species in the alloy. The electronegativity of an element is a quantity derived from experiment or theory and is not a well defined property of an element. However, the large number of correlations (Rother and Bomke 1933, Gordy and Thomas 1956, Inglesfield 1969, Hodges and Stott 1972, Sommer 1973) between other measures of charge transfer and the commonly used electronegativity scale of Pauling (1960) indicate that the concepts of charge transfer and electronegativity are viable for alloys, and that the qualitative use of Pauling's scale is justified. The purpose of the present note is to present a correlation between the electronegativities of a class of metals and a quantity not

usually associated with charge transfer, the density of bonding electrons.

In Fig. 1 are plotted the electronegativities, χ, of Pauling for the metallic elements from groups IA through IIIB of the periodic chart and the lanthanides as a function of $n^{1/3}$, where n is the bonding electron density,

$$n = Z/\Omega \quad ,$$

with Z, the number of bonding electrons per atom for the element and Ω, the atomic volume as determined from the elemental solid. (Atomic units, with $\hbar = e = m = 1$, will be used here.) The value of Z has been taken as the group number from the periodic chart, with nine and ten for the cobalt and nickel groups, respectively, and with three for the lanthanides. Values of Ω were taken from Barrett and Massalski (1966). The only elements which are metals in the solid state and are not plotted in Fig. 1 are tin, lead, francium, radium and the actinides. The other metals divide themselves into three classes in Fig. 1: 1) the metals from groups IA through VIII, aluminum, and the lanthanides; 2) the magnetic transition metals: chromium, manganese, iron, cobalt and nickel; and 3) the metals from groups IB through IIIB. The three classes are shown with distinct symbols and contain forty-four, five and nine metallic elements respectively. The linear trend of the electronegativities with $n^{1/3}$ for the first class of metals can be seen in Fig. 1 and constitutes the correlation mentioned above. The straight line in the figure is expressed by

$$\chi = 4.2\ n^{1/3} + .2$$

and was found by a least squares fit for the thirty metals from groups IA through VIII (excluding the magnetic transition metals) and aluminum.

The way in which the metals group themselves in Fig. 1 is perhaps more striking than the correlation itself. With respect to most properties, metallic elements are usually grouped according to whether they are transition, non-transition or rare earth metals. The non-transition metals are commonly treated with the nearly free electron approximation, (Harrison 1970) so that a Fermi wave vector may be defined as

$$k_F = (3\pi^2 n)^{1/3}$$

In this case, it might be expected (Inglesfield 1969) that the stronger the ionic potential of an atom of an element, the better is the ability of the atom to attract charge to itself, i.e., the larger the electronegativity. Similarly, a strong ionic potential might be expected to localize or cause a contraction of the bonding charge when a metal is in the elemental state. For these metals one would then expect a correlation between electronegativity and free electron density, n, or some other measure of electron density, like k_F. A calculation (Lang and Kohn 1971) of another parameter measuring the ability of atoms of an element to attract charge (or, actually, give up charge), the work function, has in fact yielded this qualitative result. The transition and rare earth metals cannot be treated with the nearly free electron approximation, so more complicated models must be used for these metals. As can be seen in Fig. 1, the metals do not divide themselves up according to whether or not they can be

treated with the nearly free electron approximation. Instead, the non-magnetic metals are grouped according to whether they fall before or after the noble metals on the periodic chart. Thus the nearly free electron metals show two types of behavior. The alkalais, alkaline earths and aluminum have electronegativities which increase with n (or k_F) and the other nearly free electron metals have electronegativities that decrease with n (or k_F). The non-magnetic transition metals follow the first trend and the magnetic transition metals display electronegativities which are smaller than might be expected from the linear trend of χ with $n^{1/3}$. Presumably the occurrence of ferro- or anti-ferromagnetism in these elements is associated with the ability to attract bonding charge to themselves that atoms of these elements display. The rare earth metals fall into the first class above. What is of interest here is that the distinction between nearly free electron metals and transition metals is not manifested in Fig. 1.

Another point about Fig. 1 concerns the independence of the variables used to discuss the effect of charge distribution on the phase stability of alloys. These variables (Hume-Rothery 1967, Barrett and Massalski 1966) are the size, valence, and electronegativity of an element and are used to parameterize the three principal determinants of phase stability, the size effect, the electron-atom ratio and the electrochemical effect, when the element is a constituent of an alloy. For the first class of metals mentioned above

$$\chi \cong 2.6 \frac{Z^{1/3}}{R_A} + .2$$

with R_A the atomic radius and $\Omega = 4\pi R_A^3/3$. For the forty-four elements described by this relation, χ, Z and R_A are not independent, so that for alloys among this group of metals, it would appear that the size effect, electron-atom ratio and electrochemical effect cannot be treated independently. Efforts (Miedema 1973, Miedema et al 1973) to find an independent set of variables, with which phase stability can be studied, seem worthwhile.

Finally, it should be noted that there is an element of arbitrariness in the electronegativity scale of Pauling as mentioned above, and that better parameters to use for the study of charge transfer in metallic alloys may be the electrochemical potentials (Hodges and Stott 1972) or the work functions (Miedema 1973, Miedema et al 1973) of the metallic elements. Whether or not a unique electronegativity can even be assigned to an element in an alloy and whether charge transfer can be well defined at all are questions which await the unraveling of the problem of the description of metallic bonding at a microscopic level.

REFERENCES

1. Barrett C.S. and Massalski T.B., 1966 Structure of Metals 3rd ed. (New York: McGraw-Hill), p. 338.
2. Gordy W. and Thomas W.J.O., 1956 J. Chem. Phys. 24, 439.
3. Harrison W.A., 1970 Solid State Theory (New York: McGraw-Hill), p. 108.
4. Hodges C.H. and Stott M.J., 1972 Phil. Mag. 26, 375.
5. Hume-Rothery W., 1967 Phase Stability in Metals and Alloys ed. P.S. Rudman, J. Stringer and R.I. Jaffee (New York: McGraw-Hill), p. 3.
6. Inglesfield J.E., 1969 Acta Met 17, 1395.
7. Lang N.D. and Kohn W., 1971 Phys. Rev. B 3, 1215.
8. Miedema A.R., 1973 J. Less Common Metals 32, 117.
9. Miedema A.R., de Boer F.R. and de Chatel P.F., 1973 J. Phys. F 3, 1558.
10. Pauling L., 1960 The Nature of the Chemical Bond 3rd ed. (Ithaca: Cornell), p. 88.
11. Rother F. and Bomke H., 1933 Z. Phys. 86, 231.
12. Sommer F., 1973 Acta Met. 21, 1289.

FIGURE CAPTION

Fig. 1. The electronegativities of the metals according to Pauling plotted versus $n^{1/3}$.

● - Metals from groups IA-VIII and aluminum.

△ - Cr, Mn, Fe, Co, and Ni.

□ - Metals from groups IB-IIIB.

The box represents the lanthanides.

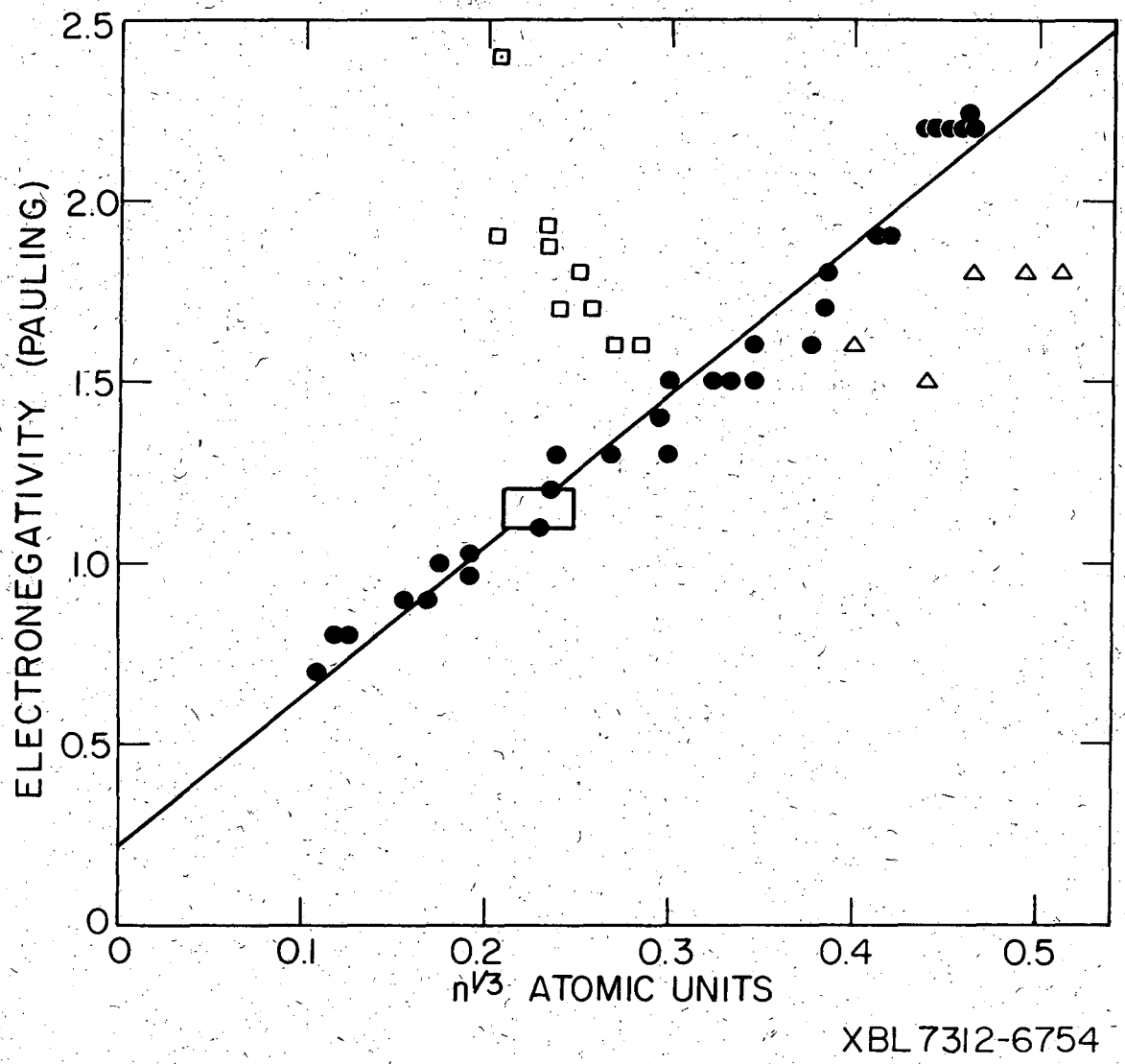
2.5
2.0
1.5
1.0
0.5
0
ELECTRONEGATIVITY (PAULING)
0
0.1
0.2
0.3
0.4
0.5
n^1/3 ATOMIC UNITS
XBL 7312-6754

Fig. 1.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720