

negligible compared with that in systems with conventional long-range order.

Thus our experiments have revealed that smectic-A liquid crystals provide an example of an anomalous dimensionality Landau-Peierls system which can be fruitfully studied experimentally, and the unusual form anticipated for the two-particle correlation functions in such systems has been directly verified. Most theoretical effort to date has been concentrated on the 2D XY model. The theory for smectic-A liquid crystals, especially near T_c , is relatively undeveloped and a significant theoretical effort is called for. On the experimental side, it should be possible to ameliorate the mosaic problems to obtain more accurate line shapes throughout the smectic phase.

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Extension of Equilibrium Formation Criteria to Metastable Microalloys

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Metastable microalloys of 25 metallic elements with beryllium have been prepared by ion implantation. The injected atoms have been found to occupy one of three sites available in the solvent lattice. A modified Landau-Ginsburg expansion using bulk alloy variables proposed by Miedema is completely successful in predicting the observed metastable-site preferences and indicates a broader applicability of these variables than was heretofore anticipated.

Defects in metals have been studied for the most part indirectly, and only in a few cases (e. g., "fast" interstitials^{1,2}) are systematic quantitative data available. By and large, the solubility (or lack thereof) of one element in another and the choice of crystal structure of compounds are determined by energy differences which are small. This is particularly true for a defect or impurity where formation energies are largely canceled by lattice relaxation. Direct prediction of alloy properties from first-principles quantum-mechanical calculations may therefore not be meaningful.

The practical approach to this problem has therefore evolved as a search for appropriate elemental configuration variables with which known data (phase diagrams, crystal structures, etc.) can be systematized, thereby providing a predictive algorithm. The classic example of this schematic-coordinate-space method is that of Darken and Gurry³ whose categorization of elements by electronegativity and atomic radius was partially successful in describing intermetallic-alloy solubilities. Similarly, Mooser and Pearson⁴ achieved reasonable success in separating different observed crystal structures for a

subset of binary AB compounds, using electro-negativity difference and average principal quantum number as parameters. More recent advances in the area of crystal-structure delineation are represented by the work of St. John and Bloch⁵ and Machlin *et al.*,⁶ who realized excellent separation of various structure classes by utilizing parameters derived from the orbitally dependent atomic radii of Simons and Bloch.⁷ An analogous advance with regard to binary alloys can be recognized in the work of Miedema and co-workers,⁸ who developed thermochemical parameters for the elements with which signs of the heats of formation of over 500 alloy systems have been successfully predicted. The quantum justification, based on the Simons-Bloch radii, for the Miedema parameters has been provided by Chelikowsky and Phillips.⁹

A commonly held preconception with respect to all of the above categorization schemes is their sole applicability to systems in thermal equilibrium. In this Letter we will show, by applying the Miedema scheme to data collected for *metastable* microalloys of beryllium, that this preconception is unfounded and that the breadth of applicability of the elemental configuration variables may be considerably wider than heretofore anticipated.

Our data base derives from a series of measurements on beryllium metal containing dilute concentrations of various metallic impurities.¹⁰ The impurities were introduced by ion implantation, a procedure capable of forming a large number of metastable structures which are inaccessible by traditional metallurgical methods.¹¹ The implanted atoms come to rest within the host metal lattice where they are constrained to choose, in an extremely short time,¹² a lattice position which represents the most energetically favorable host-impurity configuration available *locally*. Because samples were prepared at room temperature where processes such as long-range diffusion to form segregated precipitates are not operative, the "freezing-in" of metastable atomic arrangements becomes likely.

Fortunately, two artifacts of the implantation process which plague similar investigations in other host metals are not present in Be. First, as the massive implanted impurity atom slows down in the matrix, it is kinematically impossible for a replacement collision to occur at the end of range.¹³ This is simply a result of the low mass of Be. Thus an artificially high fraction of substitutional impurity arising from the

ballistics of slowing down will not be present. Second, there is a very low probability that lattice defects created by the implantation process itself will interact with the impurity in order to confuse the micrometallurgical issue. Again, the low mass of Be is helpful in quaranteeing a minimum defect density in the collision cascade because of the relatively high energy and long range of Be knockons and the defects so created (primarily vacancies near the impurity path) are not highly mobile at room temperature. The latter is a consequence of the relatively high temperature¹⁴ ($\sim 350^\circ\text{K}$) at which stage-III annealing in Be is observed. Thus we have confidence that the final impurity-host coordinations are truly representative of the chemical or metallurgical propensities of the species involved.

The reported data on these systems¹⁰ consist of impurity lattice-site determinations by the ion-beam channeling technique.¹⁵ Each implanted impurity was found either to occupy the regular substitutional lattice sites (s) of Be or to be trapped in one of the two most likely interstices of the lattice,¹⁶ viz., the octahedral (o) or tetrahedral (t) interstitial space. In the following analysis, we have included points for the host element Be and elements which were not investigated experimentally but which are known to be soluble¹⁷ in Be to at least 0.01 at.-%.

Initially we attempted to analyze s -, o -, or t -site preferences in terms of the parameter $r_s = (\frac{3}{4}\pi N)^{1/3}$, where N is the conduction-electron density of the impurity species in its elemental metallic form and r_s is measured in Bohr radii. This variable is the basis of nearly-free-electron theories of metallic properties, but there is little or no correlation between the observed site preferences and r_s . This is perhaps not surprising, because the free-electron theory is known to give a good description¹⁸ of metallic properties (such as work functions) only for alkaline and alkaline-earth metals (represented by Cs and Ba in our survey); it fails for other simple metals and for transition metals.

Our next attempt utilized the traditional metallurgical coordinates of Darken and Gurry³; these are shown as configuration coordinates in Fig. 1. Based primarily on atomic size, a rough separation of substitutional and/or soluble cases from interstitial cases is obtained. The observed separation is, however, not clear cut and thus no separation of octahedral vs tetrahedral interstitials is realized. This partial success, however, encourages one to search further for more appro-

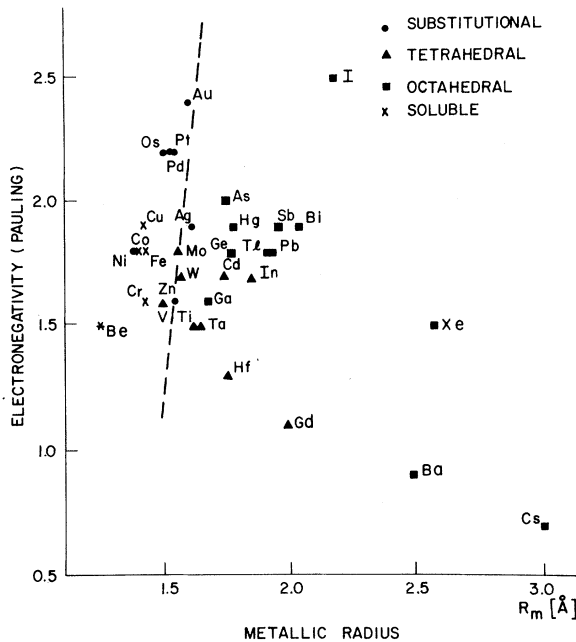


FIG. 1. Darken-Gurry plot for metastable Be microalloys. The ordinate is the Pauling electronegativity of the element and the abscissa is the metallic radius derived from the molar volume. Symbols are identified in the legend. The dashed line shows the approximate division of substitutional and interstitial impurities.

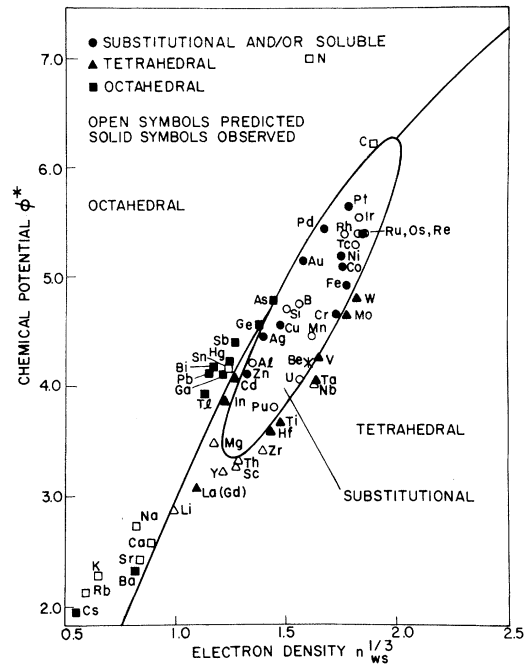


FIG. 2. Miedema plot for all tabulated elements including most of those from Fig. 1. Coordinate values are from Boom *et al.* (Ref. 8). Solid symbols (identified in the legend) are experimental data and open symbols are predictions. Coordinates for Al, Ga, In, Ca, and Cd have been slightly adjusted based on a critical review of Miedema's original data base. The changes in Al, In, Ca, and Cd do not affect the quality of Miedema's fits and our change in the Ga coordinates substantially improves agreement with phase-diagram data.

priate structural variables.

The scheme of Miedema and co-workers⁸ is a natural one to try. Miedema's parameters, ϕ^* and n_{ws} , are related, respectively, to the electronic work function of the elemental metal and to what is believed to be the electron density in the metal at the boundary of the Wigner-Seitz cell. In the cellular model of the binary alloy, a difference in ϕ^* between constituents results in a charge transfer across boundaries between dissimilar cells and provides a negative contribution to the heat of formation. A difference in n_{ws} , on the other hand, implies the need to expend energy in order to smooth a discontinuity in electron density at that boundary, thus contributing a positive term to the heat of formation. A more macroscopic interpretation of n_{ws} relates it to the surface tension of the elemental liquid metal.^{19,20} In practice, Miedema has determined the two elemental variables ϕ^* and n_{ws} for more than 50 metallic elements by fitting the signs of ΔH_f for more than 500 binary metallic alloys with a formula of the form

$$\Delta H_f = -P(\Delta \phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 \quad (1)$$

with the constant factors $P, Q > 0$. Inspection of Fig. 2, where these coordinates are used, shows immediately that *s*, *o*, and *t* sites lie in separate domains of a Miedema plot. The high degree of success evidenced here demonstrates that this parametrization is applicable to the metastable configurations represented by the data. It implies that inherent in these parameters are not only measures of the energies involved in equilibrium alloys, but also those involved in the local lattice relaxation around impurities, or for that matter defects in general. To make this separation more quantitative we use the Miedema coordinates (relative to the Be host lattice)

$$\begin{aligned} x_1(A) &= \phi^*(A) - \phi^*(\text{Be}), \\ x_2(A) &= n^{1/3}(A) - n^{1/3}(\text{Be}) \end{aligned} \quad (2)$$

in a modified Landau-Ginsburg expansion of the site-energy differences for each element *A* (in

TABLE I. Derived values for parameters of Eq. (4) and the curves of Fig. 2.

Sites	a_{11}	$a_{12} + a_{21}$	a_{22}	b_1	b_2	c
t	-1.80	11.91	-24.04	1.95	-6.34	0.16
o	-1.77	11.71	-23.79	1.81	-5.87	0.28

units of eV/g atom) as follows:

$$\Delta H_f^{\alpha t} = \Delta H_f^s + N^{\alpha t}, \quad (3)$$

$$N^{\alpha t} = \sum_{i,j=1}^2 a_{ij}^{\alpha t} x_i x_j + \sum_{i=1}^2 b_i^{\alpha t} x_i + c^{\alpha t}. \quad (4)$$

The forms of Eqs. (3) and (4) mean that the site-energy differences remain small, i. e., the same cancellation which is implicit in ΔH_f^s itself is maintained in $\Delta H_f^{\alpha t} - \Delta H_f^s$. Using Miedema's units for φ^* and $n_{WS}^{1/3}$, we found the expansion parameters given in Table I. With these parameters the boundaries of site regions are found as shown in Fig. 2. The substitutional region is an ellipse, and the octahedral and tetrahedral regions are separated by a hyperbolic contour which passes through the substitutional region.

In view of the long-range strain fields associated with point defects in metals (corresponding to abundant relaxational degrees of freedom), the calculation of our site-energy parameters from a microscopic model does not seem feasible at present.²¹ The isotropy of the Miedema-model variables is exemplified by the finding⁸ that n_{WS}^2 is strongly correlated to the ratio of bulk modulus to molar volume. It is likely therefore that an alternative approach to adjustments for local structural properties may be found in a consideration of the shear elastic constants of the host lattice.⁹ The present methods can also be used to systematize the activation energies of "fast" interstitials in other close-packed hosts such as Pb.⁹

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Direct Electron-Diffraction Evidence of Charge-Density-Wave Formation in NbSe₃

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In NbSe₃ one-dimensional diffuse scattering was observed above 140 K and the satellite spots at a lower temperature. They correspond to the Kohn anomaly and the superlattice coupled with charge-density wave, respectively. The superlattice was found to be incommensurate, with the period $a' = a$, $b' \approx 4.1b$, and $c' = c$.

Recently, the transition-metal trichalcogenides MX_3 (M : Nb, Ta; X : S, Se) have been the subjects of several investigations.¹⁻⁶ These needle-shaped materials have the chain structure of the transition-metal atoms surrounded by the chalcogen atoms along the needle axis. The distance between metal atoms along the chain is much shorter than the interchain distances. Therefore the interactions between chains seem to be weak and one-dimensional behavior is expected in MX_3 .

One of the MX_3 family, NbSe₃, is characterized by two cusps in the temperature variation of the electrical resistivity along the b axis (needle axis) at 59 and 143 K. These anomalies have been explained by assuming the formation of a charge-density wave (CDW).¹⁻³ Especially the suppression of the two peaks in the resistivity by strong electrical fields is explained as Zener breakdown across the very small gaps at the Fermi surface induced by the formation of CDW.³ In this Letter we present the first direct evidence of CDW formation, by electron diffraction above 130 K.

NbSe₃ was synthesized by direct reaction of Nb and Se without carriers. The morphology and the resistivity anomalies of our crystals were the same as those reported by Haen *et al.*² The residual resistivity ratio was ~ 70 . It was found from x-ray diffraction studies with both the precession camera and the counter method, that the $(0k0)$ reflections were missing when $k = 2n + 1$. This extinction rule indicates that the space group of NbSe₃ is either $P2_1$ or $P2_1/m$, which have higher symmetry than Pm given by Meer-schaut and Rouxel.⁴ It seems that the presence

of the 2_1 screw axis along the needle axis is a common feature of MX_3 .⁷⁻⁹ The electron diffraction of NbSe₃ was performed with the acceleration voltage of 100 kV. The sample holder was kept at 130 K. But the temperature of the individual crystal may be slightly higher as a result of irradiation by the electron beam, though a heat link to the sample holder would release some of the heat.

Figure 1 shows the b^*-c^* plane of the reciprocal space above 140 K. The anomaly in diffuse scattering can be clearly seen to be one-dimensional. The position of this one-dimensional anomaly along the b^* axis is $(0.244 \pm 0.004)b^*$, which is a little smaller than the commensurate value of $0.25b^*$. This incommensurate streak

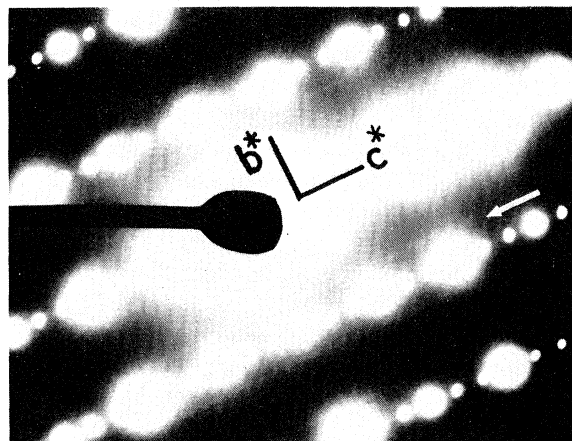


FIG. 1. Electron diffraction pattern of NbSe₃ above 140 K, showing one-dimensional anomaly in diffuse scattering (marked by arrows).