INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

H4.SMR/167 - 11

SCHOOL ON PHYSIC IN INDUSTRY

27 January - 14 February 1986

PHYSICS IN METALLURGY

presented by

C.A. WERT
Department of Metallurgy
University of Illinois
Urbana, IL 61801
U.S.A.

These are preliminary lecture notes, intended for internal distribution to participants only.

C.A. Wert
Univ. of Illinois, Urbana

Education: Physics & Materials

Teacher

thermodynamics
Diffusion + Kinetics
Author: Textbook
Physics of Solids

Editor:
with Rustum Roy
Penn State
"Journal of Materials Education"

Metals
Ceramics
Polymers

Wood
Concrete
Composites

Research

Plasticity
↓
Diffusion + Defects
↓
Radiation Damage
↓
Compounds in alloy Systems
↓
Chemistry of Soils
↓
Structure of Coal + Oil Shale
↓
Solar Cell Materials

Topics:

1. Introductory Comments
2. Examples (Physics Related)
   a. Phase diagrams
   b. Acoustical Properties
      Sound propagation
      Absorption

Break

---

   c. Magnetism
   d. Strength of alloys
3. Brief summary

METALLURGICAL "NEEDS"

1. Understanding of crystal structure of pure elements.
2. Principles of alloying.
   Role of electronic structure of individual elements.
   Role of relative atomic sizes.
   Role of position in periodic table.
   THE HUME-ROTHERY RULES: DO THEY HAVE BASIC VALIDITY?
3. The elastic moduli. Their relationship to force constants.
   How do you control the elastic limit?
4. Plasticity of metals and alloys.
   Engineering features. Balance between strength and ductility.
   Basic features. Is basic study of dislocations important?
5. Corrosion. Macroscopic features vs microchemistry.
6. Boundaries. Surfaces and grain boundaries. Twins.
7. Transformations. Diffusion controlled. Precipitates.
   Coherent and incoherent interfaces.
   Diffusionless. Martensites. Memory alloys.
   Thermodynamic equilibrium.
8. Reaction rates. Relative role of diffusion and nucleation.
9. Embrittlement. Grain boundary and bulk effects.
10. Surfaces. Crystallographic and Electronic Structure
11. Interfaces. Structure. Thermodynamic Properties. Impurities.
12. Defect Structures. Superlattices.
13. Failure. Brittle fracture. Fatigue. Creep.
14. Structure: Crystals. Compounds. Amorphous Materials.
15. Chemistry of Fine Particles.

FUNDAMENTAL TOPICS IN PHYSICS

1. Statics and dynamics. Motions of particles.
   Elasticity. Hooke's law.
2. Thermodynamics and kinetics of reactions.
3. Relativity.
4. Electricity and magnetism.
5. Acoustics.
6. Light propagation. Lasers.
   Interaction of light with matter.
7. Atomic physics. Electron energy levels in solids.
   Fermi statistics.
8. Quantum physics. The uncertainty principle. Tunneling.
9. NMR ESR MASS SPECTROSCOPY AUGER SPECTROSCOPY
   PHOTOELECTRON SPECTROSCOPY ENERGY LOSS SPECTROSCOPY
   ELECTRON AND PROTON INDUCED X-RAY EMISSION
   RAMAN SPECTROSCOPY
10. Radioactivity.
11. Ion bombardment. Ion implantation. Channeling.
12. X-rays and gamma rays.
13. Diffraction of photons, neutrons and electrons.
14. Crystal structure. Defects in crystals.

Topics of Papers	Phys.Rev. B Jan 1, 1986
Magnetism (metals and alloys)	16
Magnetism (non-metals)	8
Phase relations	12
Diffusion	5
Acoustic effects	3
Electronic effects	5
Optical effects and properties	3
All other	11
TOTAL	63

	Phys.Rev. B Dec 15,1985
Electronic structure	26
Optical properties	14
Electronic conduction	9
Thermodynamics of compounds and alloys	8
Surfaces	8
Photons, plasmons, excitons, phonons	6
Electrical and magnetic properties	5
Defects	4
Scattering	3
Acoustical properties	3
Elastic properties	2
Amorphous materials	2
Total	96

IMPORTANT METALLURGICAL DESIGN PRINCIPLES

1. Each application must meet a number of criteria.
   Strength, corrosion resistance, ductility,......
2. The variety of possible alloys is enormous.
   Chemistry, heat treatment, deformation state,....
3. The essence of design is to make an optimal choice.
   The material is fine-tuned to provide the best
   features with long life at the least cost.

GENERAL THEOREMS FOR PHYSICISTS

1. Physicists are not good "design engineers" generally .
2. But keep in touch with the technology of your area.
3. Physicists can be valuable in making broad interpretations.
4. Keep a wide outlook. At meetings, spend half your time in sessions outside your specific area. Visit other laboratories. Listen more than talk. Change areas of work.
5. Work on both simple and complex problems at the same time.

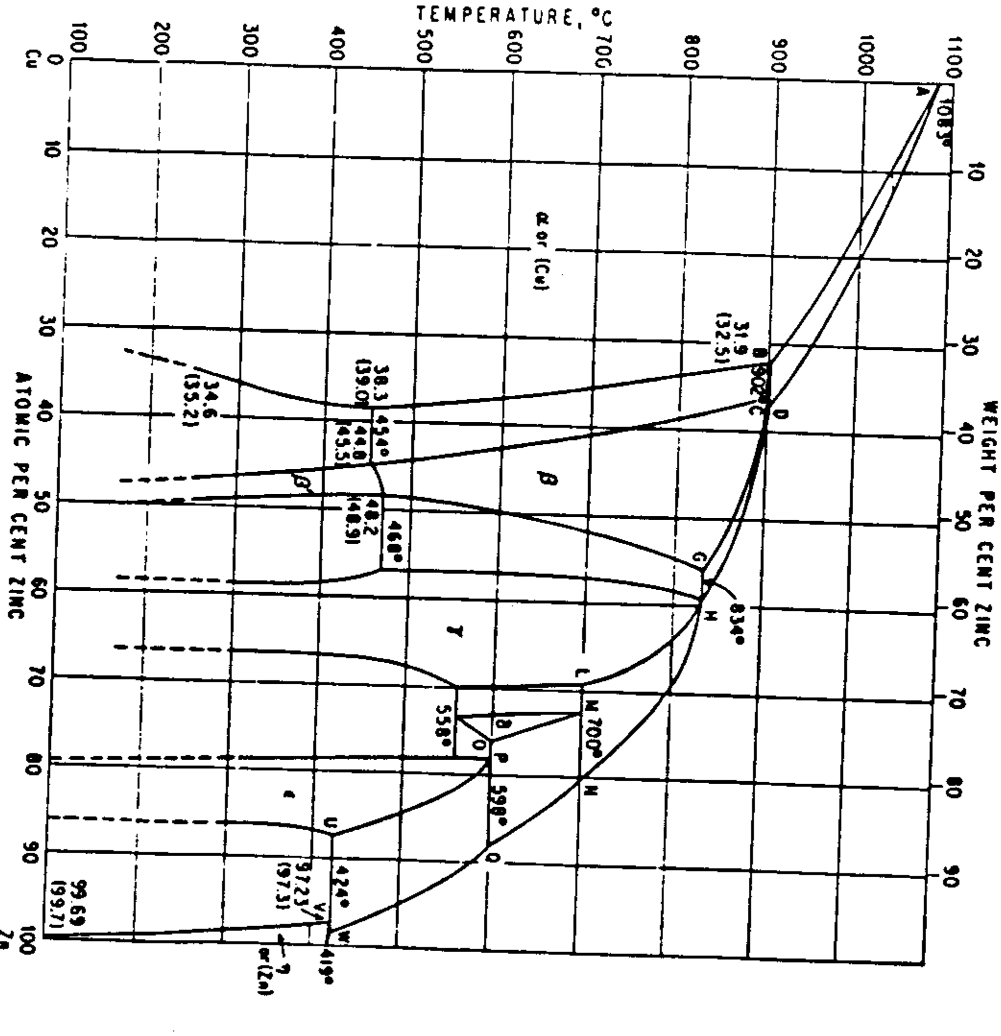


Fig. 367. Cu-Zn

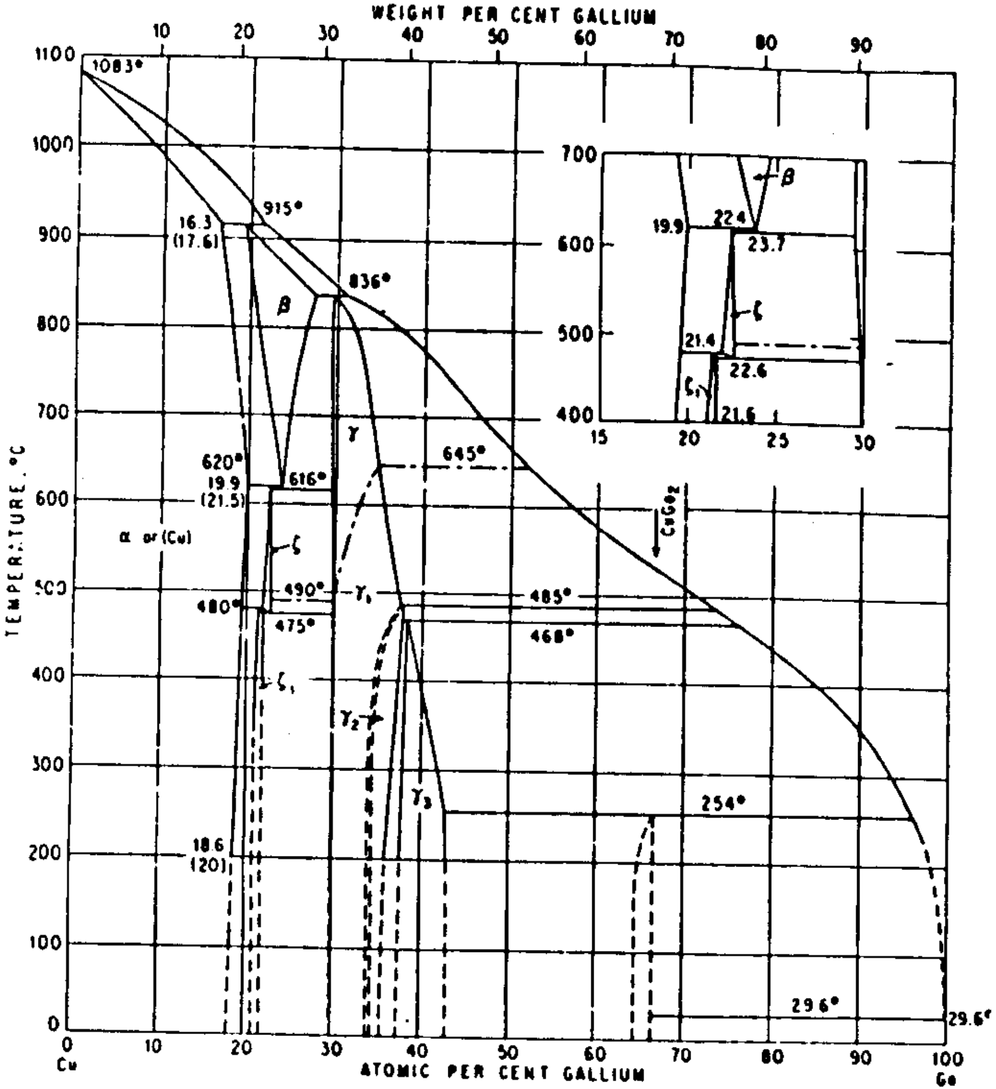


Fig. 338. Cu-Ga

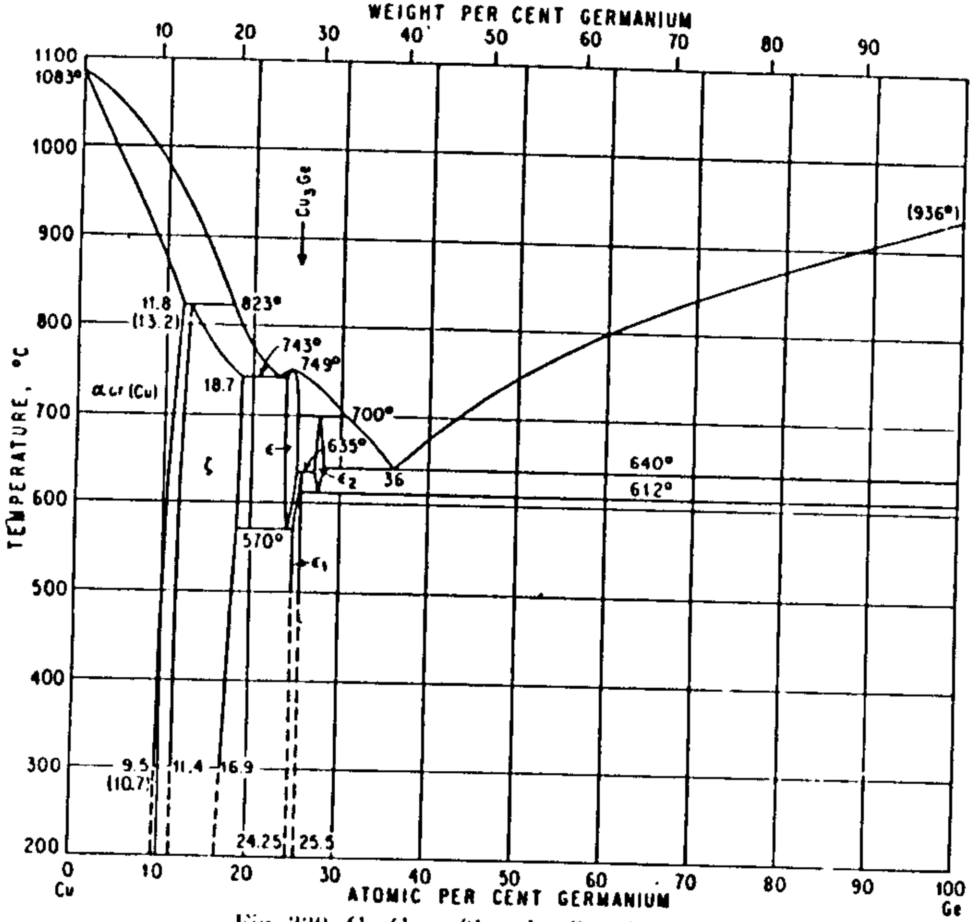


Fig. 339. Cu-Ge. (See also Supplement.)

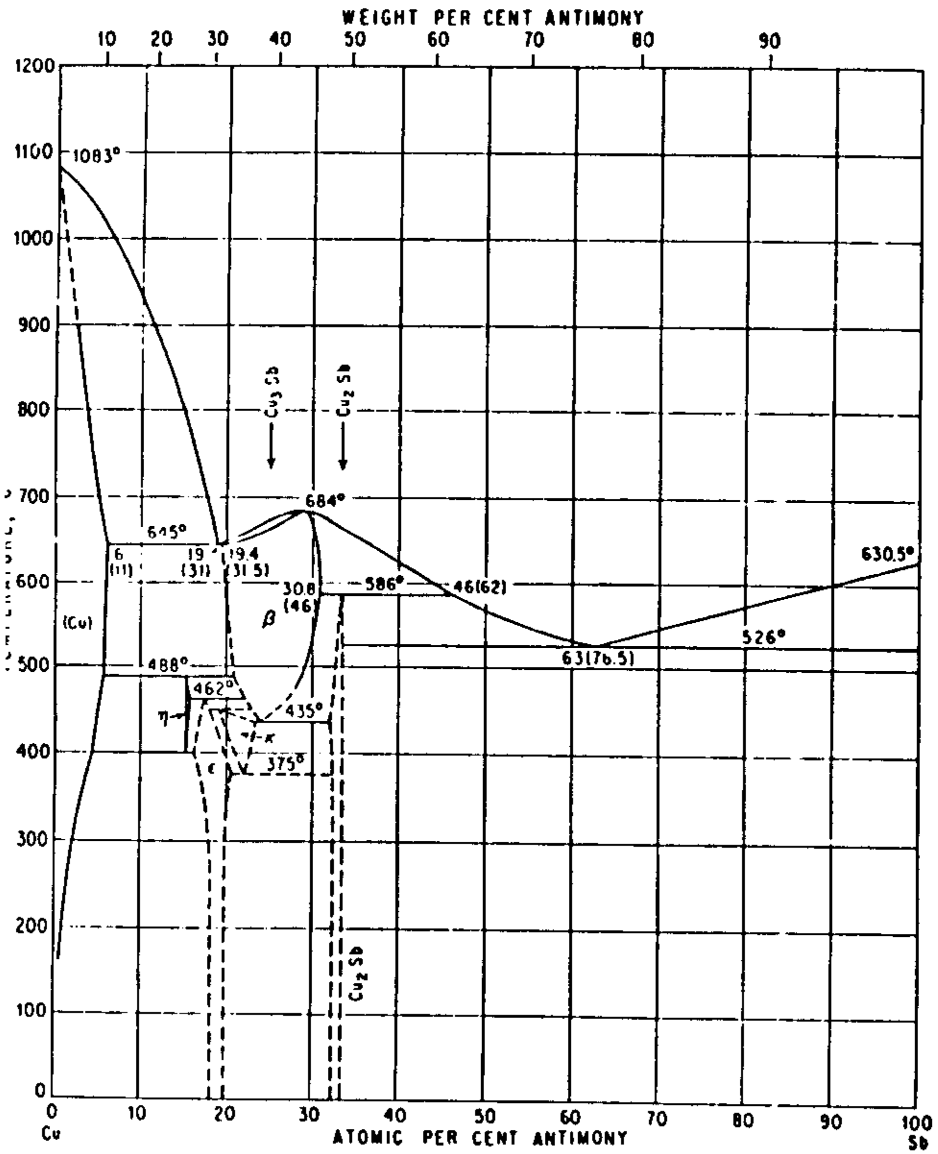


Fig. 356. Cu-Sb. (See also Fig. 357 and Supplement.)

THE HUME-ROTHERY RULES FOR ALLOYING

1. The solid solubility of one element in another becomes very restricted if the atomic diameters of the two elements differ by more than about 15%.
2. Stable compounds tend to be formed when one element is very electropositive compared with the other.
3. The amount of solid solution of elements in each other depends on their relative valency. In general, the the element of lower valency will dissolve more of the element of higher valency than vice versa.
4. For Cu, Ag and Au, compounds form at definite values of electron/atom ratios. These ratios are 3/2, 21/13 and 7/4.

References:

Atomic Theory for Students of Metallurgy
W. Hume-Rothery, The Inst. of Metals, London, 1946

Structure of Metals, C. Barrett and T. Massalski
Mcgraw Hill, New York, 1966. Third Edition.

Electronic Structure of Metallic Compounds and Alloys: Experimental Aspects. D. Sellmeyer p 83
Solid State Physics, vol 33, 1978, Acad. Press
Eds: H. Ehrenreich, F. Seitz and D. Turnbull.

The Electronic Structure of Alloys, H. Ehrenreich and L. Schwartz, Solid State Physics, vol 31, p15
Acad. Press. Eds: H. Ehrenreich, F. Seitz and D. Turnbull.

1

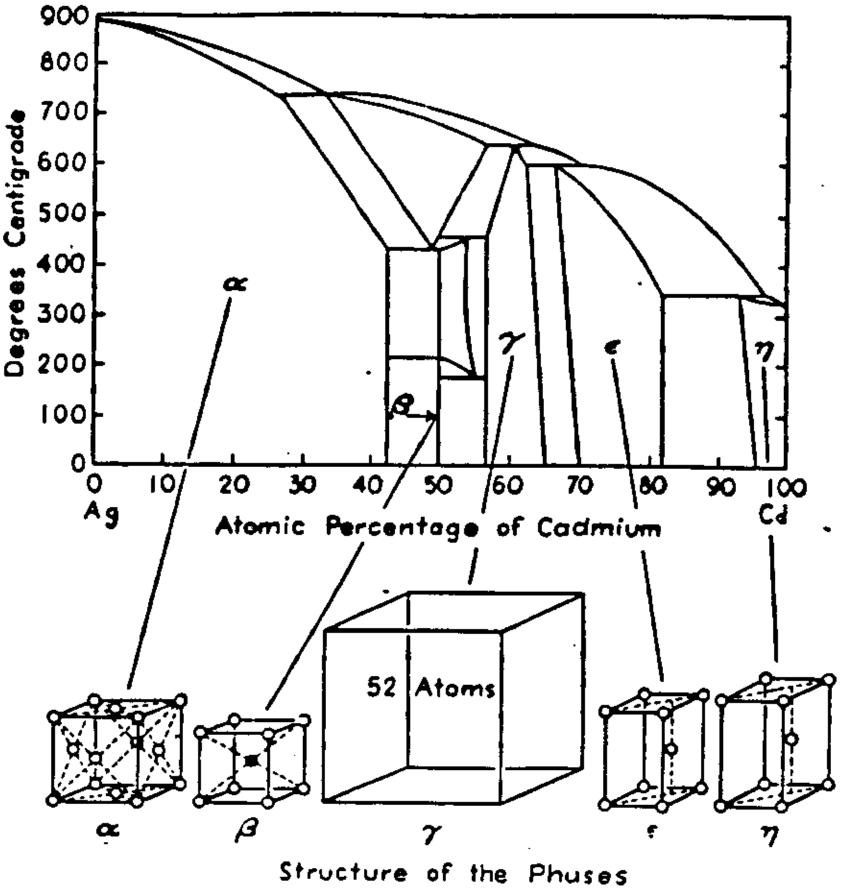


FIG. 13.—Crystal structures of the phases in the Ag-Cd system, a structurally analogous system.

13

12

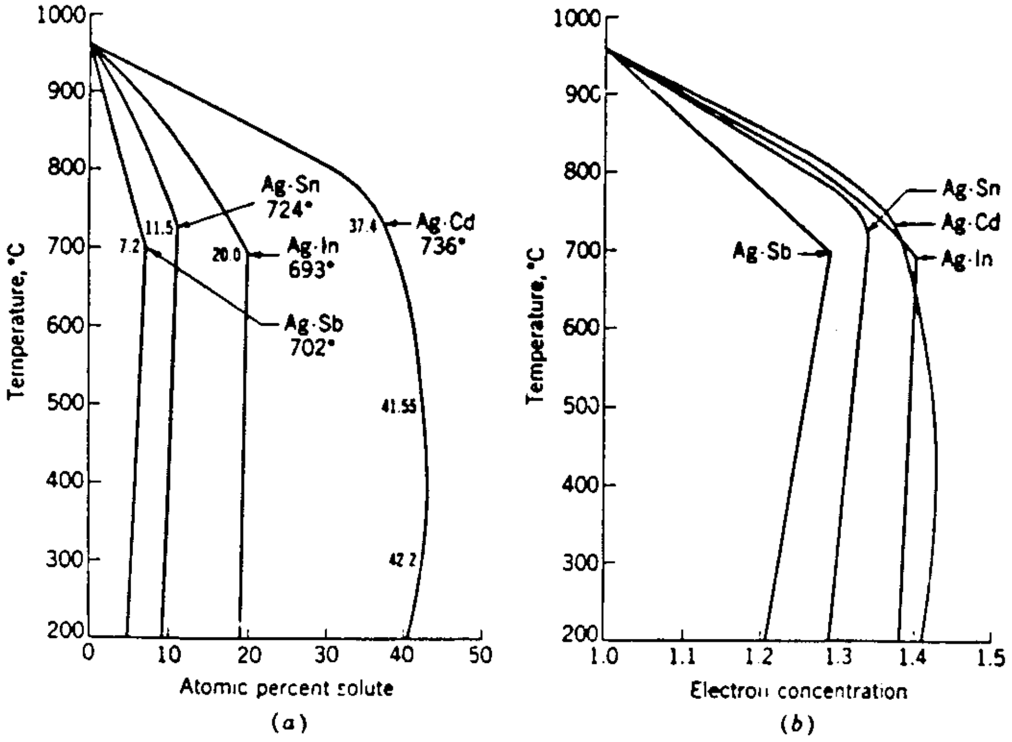
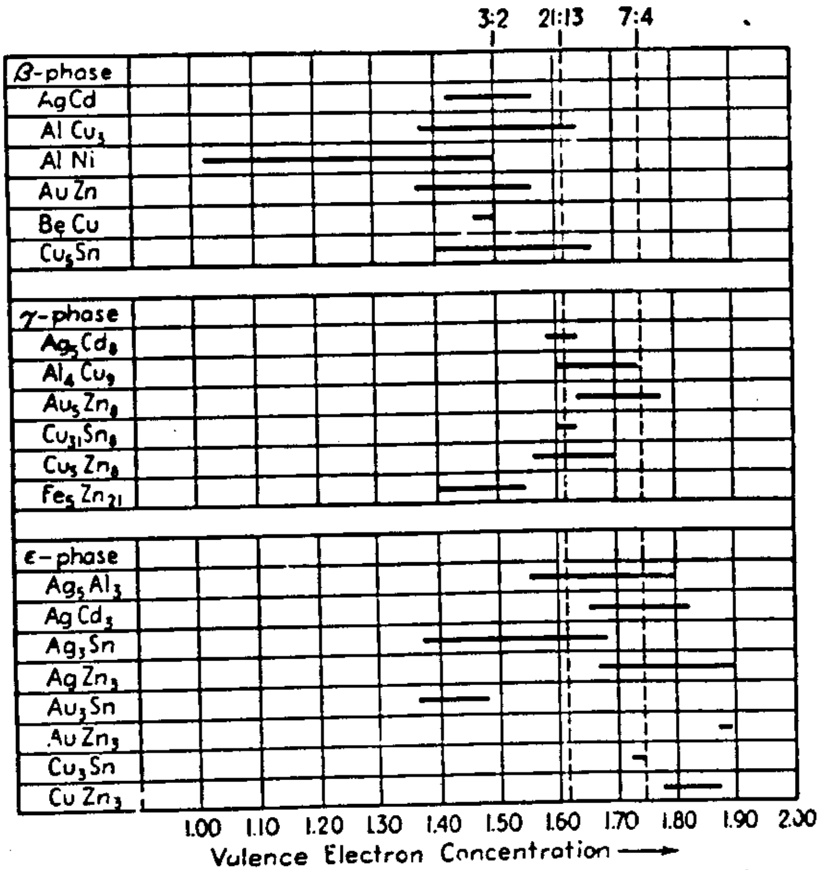


Fig. 13-2 Phase fields of primary solid solutions based on silver: (a) in terms of atomic composition and (b) in terms of e/a.



ntrations for several typical β, γ, and ε phases, compared

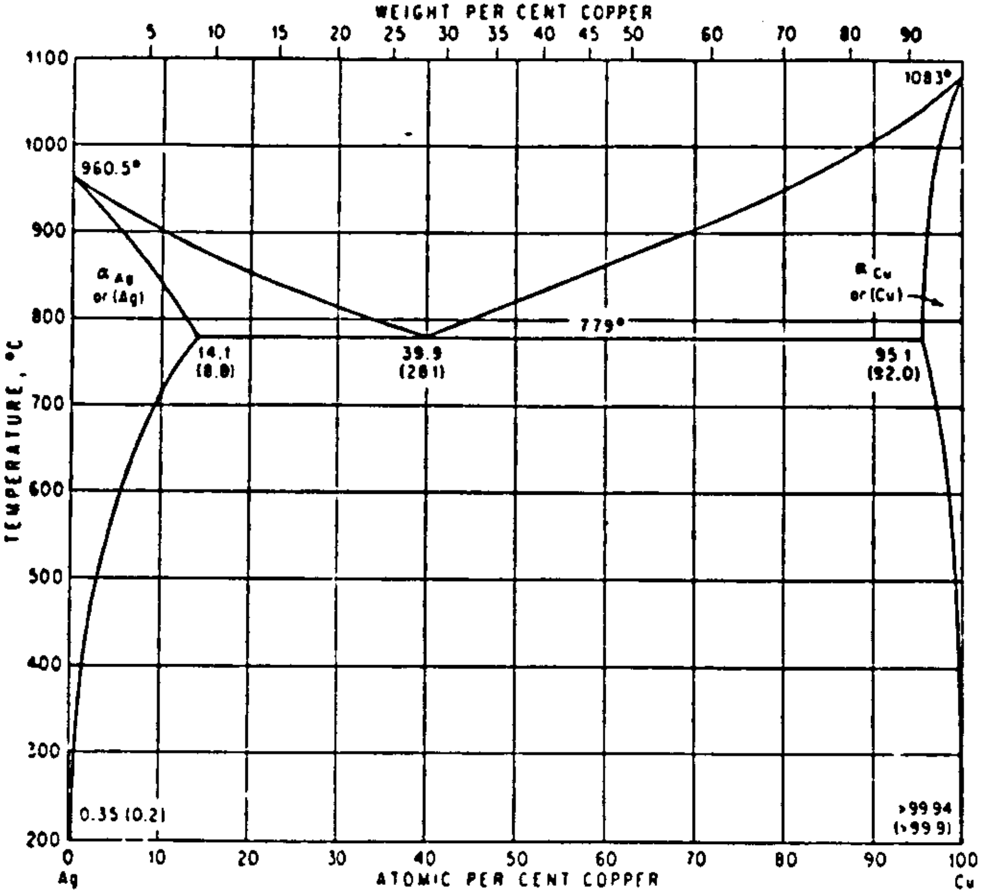


Fig. 11. Ag-Cu

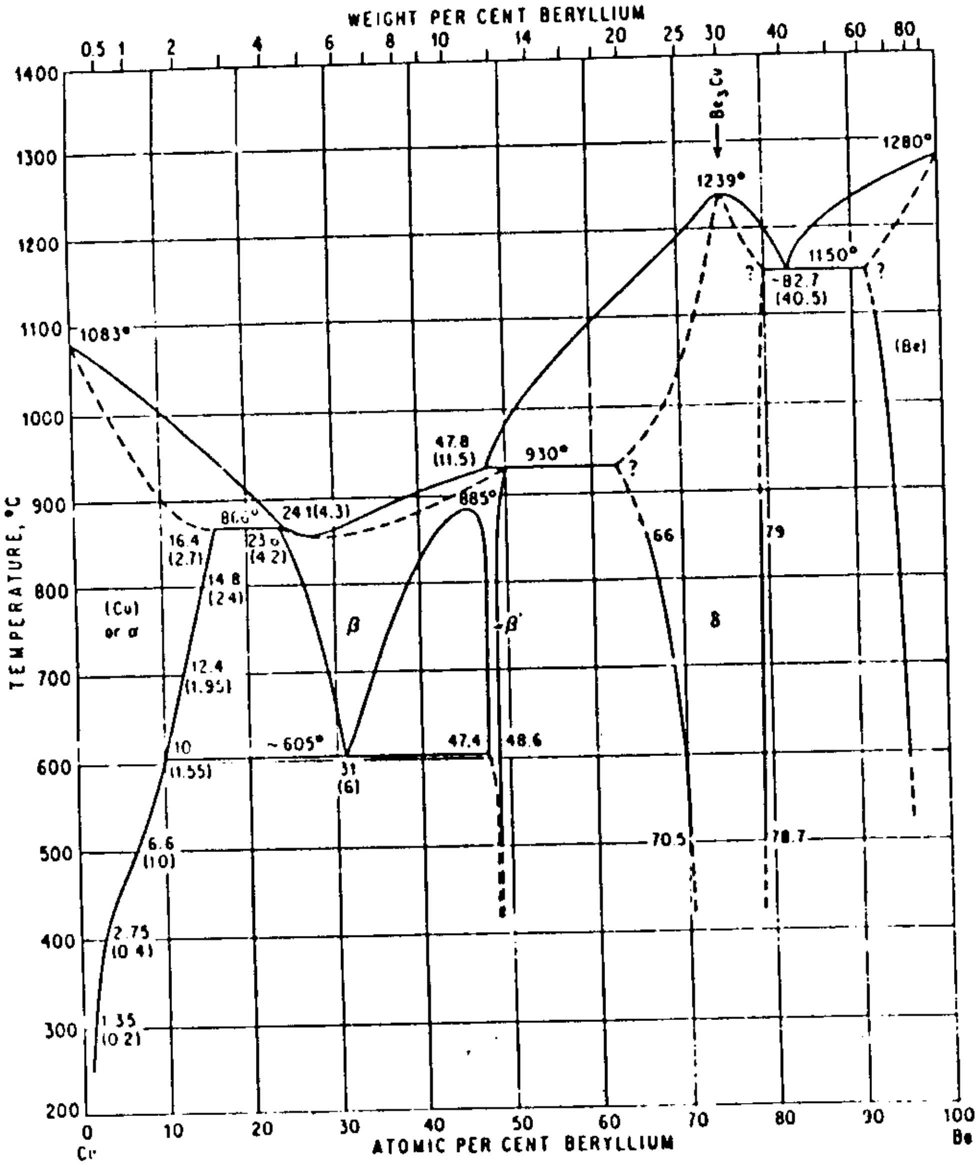


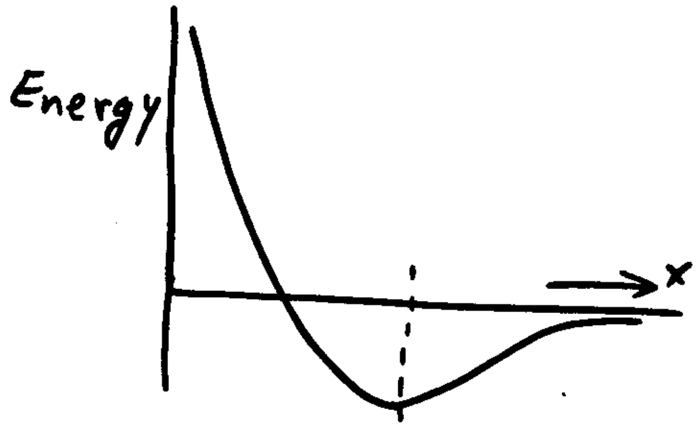
Fig. 163. Be-Cu

THE RIGID BAND MODEL

Alloys of the noble metals Cu, Ag and Au with multivalent alloying elements.
Cu + Zn, Ga, Ge or As.

Change of the Curie temperature with alloying additions. Ni + Cu

19

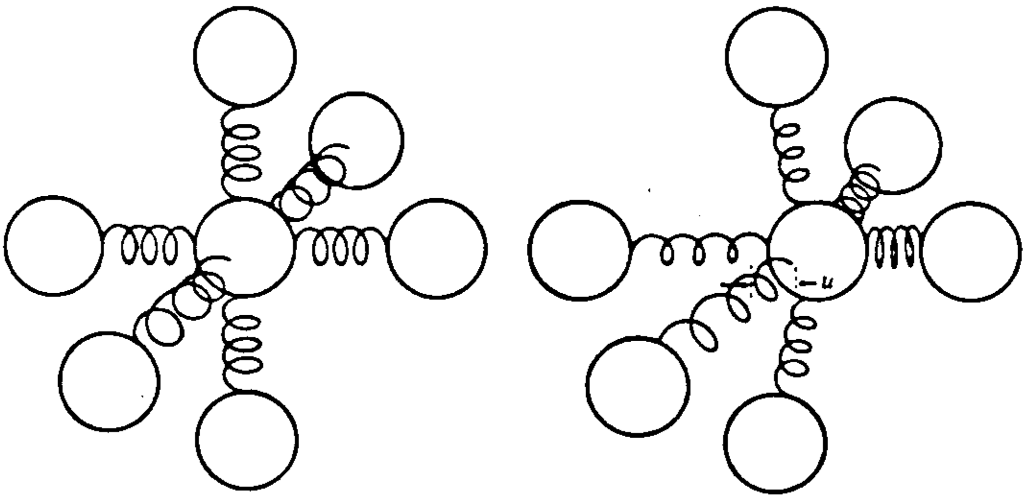


$$\text{Energy} = \frac{1}{2} A_2 (\text{strain})^2 + \frac{1}{6} A_3 (\text{strain})^3 + \cdots$$

A_2 = 2nd order constants

A_3 = 3rd order constants

18



(a) (b)

Figure 3-2 (*a*) The atom in its equilibrium position. (*b*) The atom displaced a distance *u* in the *x* direction. The springs in the *y* and *z* direction do not change their length to a first approximation.

PROPAGATION OF SOUND

Relationship to elastic properties

Measure sound velocity

$$E = \rho v^2$$

Define 2nd and 3rd order constants

Energy = 1/2 $C_{ijkl}\,\epsilon_{ij}\,\epsilon_{kl}$ 2nd

Energy = 1/6 $C_{ijklmn}\,\epsilon_{ij}\,\epsilon_{kl}\,\epsilon_{mn}$ 3rd

Corresponding terms for 4th
5th

For cubic crystals: 3 2nd
6 3rd
11 4th

Second order constants

Substance	Youngs Modulus	
1. Aluminum	70,000 MPa	10 Mpsi
2. Iron(steels)	205,000	30
3. Tungsten	280,000	40
4. Glass	70,000	10
5. TiC	350,000	50
6. Carbon fibers	560,000	80
7. Boron	520,000	60
8. Nylon	3,500	0.5

IMPORTANT FACTS ABOUT 2nd ORDER CONSTANTS

Not a structure sensitive property

Not affected much by alloying

C_{ijkl} is roughly proportional to T_m

(R.Fleisher Jour of Metals Dec. 1985)

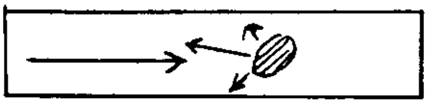
THIRD ORDER ELASTIC CONSTANTS

1. DIFFICULT TO MEASURE   DIFFICULT TO INTERPRET
2. NUMERICALLY ABOUT SAME SIZE AS 2nd ORDER CONSTANTS
   OFTEN NEGATIVE
3. IMPORTANCE FOR RELATIONSHIP TO:
   - Thermal expansion
   - Temperature dependence of 2nd order constants
   - Harmonic generation in propagation of sound waves
   - Phonon-phonon interactions
   - Lattice distortion around crystal defects

REFERENCE: Y.Hiki   Annual Reviews of Materials Science
Volume 11, page 51, 1981

SCATTERING OF SOUND FROM DEFECTS IN CRYSTALS

1. The problem. Suppose a defect is in a crystal.
   Position unknown. Size unknown. Shape unknown.
   Type unknown. Orientation unknown.
   GOAL: Using acustical measurements, specify as much as possible about the defect.



2. The experimental difficulties.
   Generating the appropriate sound wave in the solid.
   Detecting the re-emitted energy.
   Interpreting the results. Uniqueness of assignment.
3. Understanding of interaction of sound wave with defect.
   General character of the reflecting site.
   Wavelength of wave compared to the defect size.
   Mode conversion.

References: M. G. Silk, International Metallurgical Reviews
Vol.27 page 28 1982

D. O. Thompson, Ames Laboratory,
Iowa State University, Ames, Iowa, USA
Annual Conference in USA

Ultrasonics, Butterworth, London. Periodical

Jour. of Acoustical Society of America.
Includes articles on wave propagation in biological tissue.

Institute of Electrical and Electronic Engineers
See especially annual ULTRASONICS SYMPOSIUM

ACOUSTIC EMISSION

Fact: Sound waves are emitted from solids when they are stressed into the plastic range.

Goal: Use these sound waves to deduce features of the deformation process.

Principal factors:

a. What are the characteristics of waves resulting from plastic deformation?
b. How is sound generated when cracks are formed?
c. What are the problems of detection? What is the nature of the wave? What is its intensity? direction?
d. How can the measurements be traced back to location, nature and shape of the unit which generates the crack?

Reference: Wadley and co-authors.
International Metallurgical Reviews
Vol. 25, page 41, 1980

ULTRASONICS, Butterworth, London

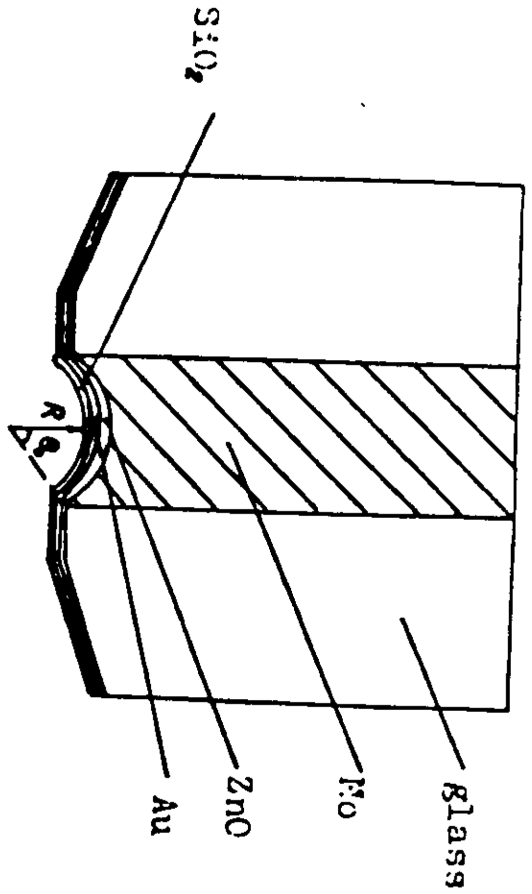


Fig 1 Design of glass-metal concave transducer

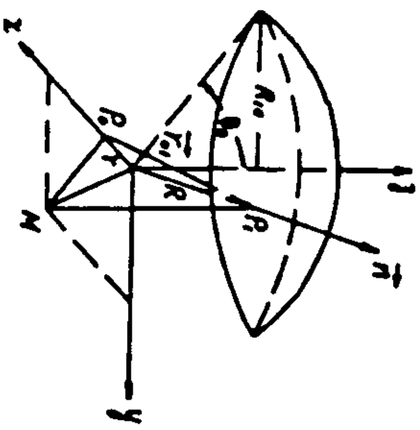
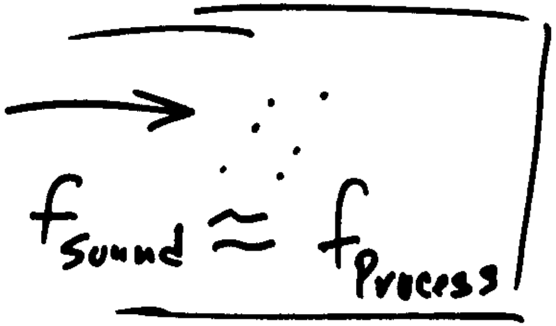


Fig 2 Diffraction geometry for concave transducer

Acoustical Energy Dissipation

1. Broad frequency response
   a. Japanese Bell
   b. Steel tuning fork
   c. Cast iron tuning fork
   d. Mg-Zr alloy
2. Narrow frequency response
   line absorption



PROTECTIVE MECHANISM

1. During Infiltration Protective Layer Forms. Intermetallic alloy of Cu-Fe-Co.
2. Shields Iron so that it does not dissolve in molten Copper.
3. After some time, Cobalt diffuses into Iron and protective layer disappears.
4. Protection disappears.

PRINCIPLES

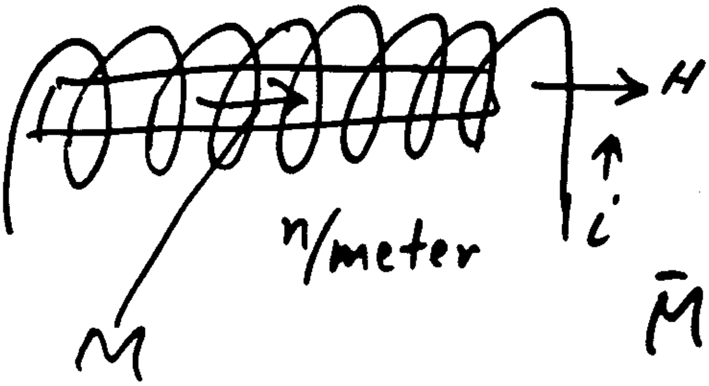
Define a magnetic field as the field about a wire carrying a current.
$H = nI$ Ampere turns/meter

If the medium is not vacuum, the magnetic flux may be different. An additional magnetization M may exist which is a function of H. $M = \chi H$ M also has units Ampere turns/meter.

Define $B = \mu H$. If the medium is vacuum, the $B = \mu_v H$.
In general, for any medium, $B = \mu_v H + \mu_v M$.
Also, for any medium $B = \mu_v \mu_r H$. Here, μ_r is the permeability relative to the vacuum value μ_v. Note that $\chi = \mu_r - 1$.

Recall three possible regimes.
- If $\chi < 1$, material is termed diamagnetic.
- If $\chi > 1$, but $M = 0$ in the absence of a field H, paramagnetic.
- If $\chi > 1$ and M has a value in the absence of H, ferromagnetic.

$$B = \mu_v M + \mu_v H$$



$$\bar{M} = \chi \bar{H}$$

ENERGIES

1. Energy of magnetization: Energy = $\int \mu_v H \cdot dM$
2. Exchange energy. Energy = f(spins on adjacent atoms). 2kcal/mol.
3. Crystalline anisotropy energy. Defined as K_1.
4. Domain wall energy. For iron about 1 millijoule/meter .
5. Magnetostriction energy. Comes from elastic strain which arises from the process of magnetization.
6. The self energy of a magnet in its own field. This is important for both transformer materials and permanent magnets.
7. Eddy-current loss in the magnetic material in the presence of an alternating magnetizating field H.

Table 18-1 Magnetic units

Factor	Mks rationalized	Cgs emu	Conversion
B	Webers/m^2	Gauss	1 weber/m^2 $= 10^4$ gauss
H	Ampere-turns/m	Oersteds	1 amp-turn/m $= \frac{4\pi}{10^3}$ oersteds
Magnetization	M, amp-turns/m	I, maxwells/cm^2	1 amp-turn/m $= \frac{1}{10^3}$ maxwells/cm^2
Permeability of vacuum	μ_v, henrys/m	$\mu'_v = 1$	
Relative permeability	μ_r	μ'	$\mu_r = \mu'$
Susceptibility	χ_m	χ'_m	$\chi_m = 4\pi\chi'_m$

The Effect of Magnetic Transformations on Phase Diagrams

By A. P. Miodownik
Department of Metallurgy
and Materials Technology
University of Surrey
Guildford GU2 5XH

Magnetic transformations are generally indicated on phase diagrams by broken lines representing the onset of magnetic ordering on cooling. Because broken lines are also commonly used where experimental results are unconfirmed or refer to unusual effects, magnetic transformations are often tarred with the same brush of uncertainty and dismissed as of secondary importance. In fact, magnetic transformation temperatures generally can be determined more accurately than many phase boundaries, because it is not possible to suppress such transformations. More importantly, the energy associated with magnetic transformations is deceptively large, and it often exceeds that released by normal phase transformations. Therefore, there can be major effects on the relative stability of various phases on passing through magnetic transformation. Table 1 indicates some of the various ways in which magnetic changes are reflected in phase transformations and lists some of the systems in which these effects have been experimentally observed.

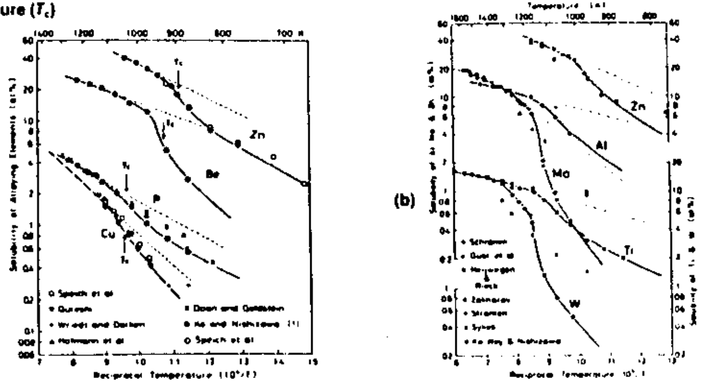
Table 1 Some Experimentally Observed Effects Caused by Magnetic Transformations on Phase Diagrams and Examples of Alloy Systems in Which They Were Observed

Alloy system	Reference	Alloy system	Reference
Changes in solubility of precipitates			
Fe-P	1	Co-Cu	2
Fe-Cu	2, 3	Co-Mo	5
Fe-Be	1	Co-W	5
Fe-Zn	4	Co-Ti	5
Fe-Co-*X*	1	Co-Al	5
Distorted miscibility gaps			
Fe-Co-Cr	6	Co-Fe-Zn	8
Ni-Au	7	Co-V	9
Changes in transus for iron-base alloys			
Fe-Cr	10	Fe-Os	7
Fe-Co	11-15	Fe-Rh	7
Changes in M_s			
Fe-Ni	12	Fe-Co	16
(Fe-Mn)		Fe-Pt	17
Transitions for second-order to first-order transformations			
Fe-Si	18	Fe-Al	19, 20
Change in stability of ordered phases			
Fe-Ni	21		

Change in Solubility of Precipitates

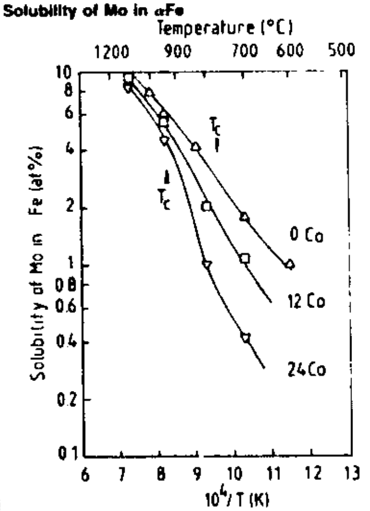
The most undeniable effect of a magnetic transition on phase boundaries is a change in solubility of a second phase, as illustrated in Fig. 1(a) and 1(b) and observed in many systems (see Table 1, "Changes in solubility of Precipitates"). It occurs whenever the Curie temperature intersects a transus line, and not only does the effect coincide with the Curie temperature, but also its magnitude is proportional to the degree of magnetization involved. This is well demonstrated by looking at the effect of cobalt additions on the solubility of other solutes (Fig. 2).

Fig. 1 Changes in Terminal Solubility Created by the Intersection of a Transus Line and the Curie Temperature (T_c)



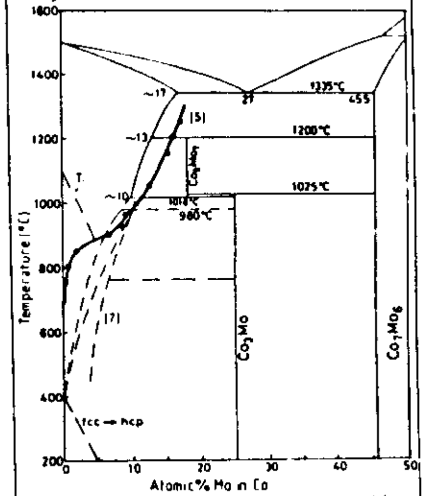
For various solutes in (a) bcc iron [8], and (b) fcc cobalt [5]. The extrapolated solubilities based on the high temperature nonmagnetic condition are shown by dotted lines to accentuate the abrupt change in the vicinity of T_c. The arrows indicate the extent to which short-range order effects allow a smooth transition between the two solubilities above T_c.

Fig. 2 Effect of Various Co Additions on the Solubility of Mo in αFe



The increased magnetism of the α phase, shown by the shift in T_c with Co content, is accompanied by a corresponding increase in the solubility anomaly below T_c [1].

Fig. 3 Terminal Solubility Curves for Co-Mo Alloys

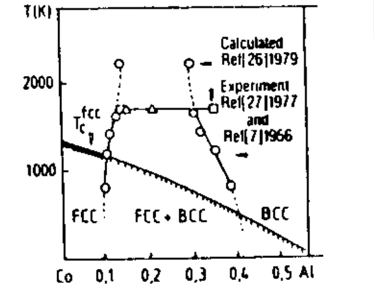


As depicted by Shunk [7] and the more recent experimental results of [5]. The heavy line represents the best calculated value consistent with the observed variation of T_c.

The energy of magnetization is generally a function of two variables, the Curie temperature, T_c, and the number of magnetic electrons, β (Bohr Magnetons), involved. Only the former is usually available in phase diagrams, but fortunately, the two factors are often proportional to each other. Therefore, it is possible to gauge the likely magnitude of an effect simply by looking at the magnitude of the Curie temperature. Because there can be a continuous variation in the degree of long-range order (chemical or magnetic), the transformation is spread over a range of temperature below T_c, and because there also is usually a substantial degree of short-range order, there is an equivalent (but smaller) effect just above T_c.

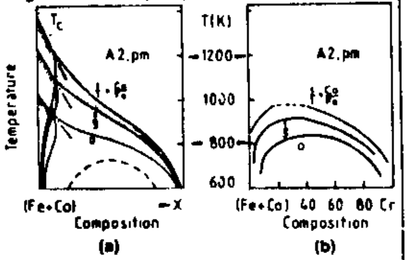
If the magnetic parameters are known, it is possible to calculate the expected changes in solubility [8, 22], and good agreement generally has been obtained between calculated and experimental results. Because calculations of the magnetic energy have been extensively reviewed elsewhere [8, 10, 11, 23-25], it is not proposed to deal with them in this article. They do, however, support the reality of the effects, and the nature of the changes to be expected. *This has the consequence that the location of phase boundaries in systems containing magnetic phases may have to be reconsidered.* Figure 3 shows part of the Co-Mo diagram as depicted by [7], and it shows the expected form of the relevant transus if magnetic effects are included. Experimental data [5] confirmed the calculated position, and a similar situation has been shown to exist in the Co-Al system [26, 27] (Fig. 4).

Fig. 4 Comparison of Experimental and Calculated Transus Lines in Co-Al Alloys



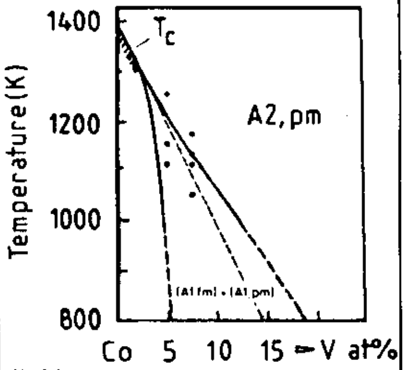
The calculations suggest that an anomaly is to be expected in the (fcc + bcc)/bcc transus as well as in the terminal solubility

Fig. 5 Miscibility Gap in Co-Fe-Cr Alloys



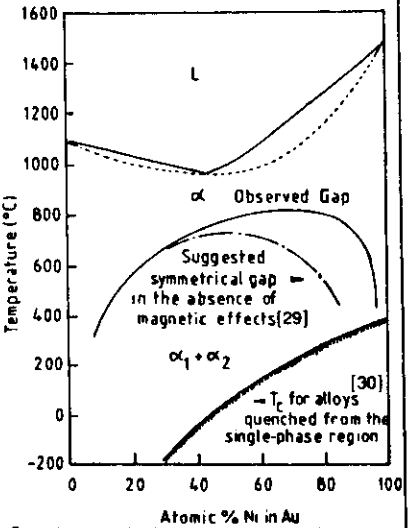
(a) Theoretical form of a miscibility gap in a binary magnetic system following [1], and (b) the shape of the miscibility gap found experimentally in Co-Fe-Cr alloys by [6]. It is difficult to find an example in a binary system because of interference by competing phase transformations

Fig. 6 Experimental Confirmation of a Continuous Transition Between First- and Second-Order Transformations in Co-V Alloys



After [9], probably the most telling illustration of unexpected effects due to magnetism. Points represent experimental results, and lines, the calculated equilibria

Fig. 7 Relation Between Asymmetry in the Miscibility Gap of Au-Ni Alloys [7] and Corresponding Asymmetry of Magnetic Characteristics in This System



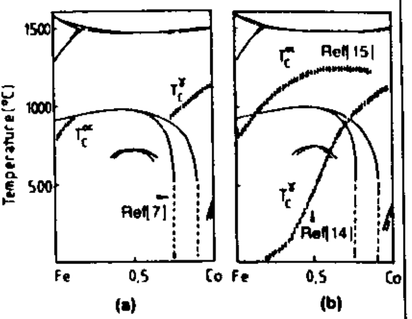
Few other property changes can arise so suddenly in the middle of an alloy system that does not exhibit compound formation.

Distorted Miscibility Gaps

It should now be clear that magnetic effects can not only displace transus lines, but also produce unusual changes in their shape. Theoretical predictions [8, 28] suggest that a symmetrical miscibility gap would be distorted, as shown in Fig. 5(a); many variants can arise depending on the degree of 'normal' chemical or elastic immiscibility. It is not easy to find experimental confirmation of such effects in binary alloys, because many of the systems containing magnetic components tend to have stable intermetallic phases that obscure the inherent immiscibility between terminal solution phases. However, it has proved possible to examine the metastable immiscibility gap in the Co-Fe-Cr ternary system [6] (Fig. 5b), which broadly confirms the expected asymmetry. It should be noted that, apart from the asymmetry, Fig 5(a) shows another apparently anomalous feature, namely a continuous transition between the Curie temperature (which is a second-order transformation) and the boundaries of the immiscibility gap (which denote a first-order transformation). This effect has been demonstrated experimentally in the Co-V system [9] (Fig. 6) and emphasizes why one should not relegate second-order transformations as being of secondary importance.

It is fairly certain that the asymmetric miscibility gap in the Ni-Au system (Fig. 7) is due to magnetic effects, but the mechanism cannot be the same as that invoked for Fe-Cr or Fe-Co-Cr alloys because the Curie temperature of nickel is far too low in relation to the top of the gap. Several alternative explanations have been invoked, which depend on different models for the state of nickel ions in gold solutions [29, 31]. A re-examination of the change in gap symmetry in various Au-Ni-*X* ternary alloys currently is being conducted in order to differentiate between various suggestions.

Fig. 8 Fe-Co Diagram



The Fe-Co diagram as normally depicted with (a) only partial representation of Curie temperatures, and (b) the metastable continuation of these critical temperatures. Note the sudden drop in the $(\alpha + \gamma)$ transus when the value of $T_c(\gamma)$ begins to approach the value of $T_c(\alpha)$

Anomalous Shapes for the α/γ Transus in Iron Alloys

Dramatic changes in the shape of phase boundaries also can occur without any obvious connection to the magnetic properties of the system. This is best exemplified by looking at the Fe-Co system, in which the (α and γ) field (Fig. 8) is clearly unexplainable by reference to the chemical or elastic properties of iron and cobalt.

This system differs from the previous examples in that both phases show strong magnetic effects, and it is, therefore, the *relative* strength of the magnetic contributions in the α and γ phases that matters. Magnetic information normally is presented only for stable phases, and in this particular situation does not give a very good indication of the importance of the magnetic factor for more than a very small region at either end of the diagram (Fig. 8a). However, it is possible to measure T_c^γ in retained γ over a wider range of compositions by using quenched powders [14] and, likewise, to estimate T_c^α by extrapolating magnetic measurements for α alloys to higher temperatures [15]. With this extra information, it is possible to see (Fig. 8b) that the initial rise of the α/γ transus is consistent with the rise in the Curie temperature of the γ phase and, more interestingly, that the spectacular fall in the α/γ transus at higher cobalt contents is associated with the rapid rise of T_c in the γ phase. The relative phase stability of α and γ, of course, also are affected by many other factors, but there is little doubt that the relative magnetism of the two phases is the dominant factor in this system. Pursuing this argument further, it follows that the α/γ transus in *all* iron-base alloys is affected by the way the solutes differentially affect the magnetic properties of the bcc and fcc phases; in many instances, general size factor or elastic effects tend to obscure the magnetic contribution.

There is no doubt that if bcc iron were not ferromagnetic, α iron would not be the stable room temperature allotrope. The onset of ferromagnetism causes the free energy curves for the α and γ phases to run almost parallel and very close together for several hundred degrees, so that not only is the A_3 transition very strongly controlled by magnetic forces, but also the actual difference in energy between α and γ iron becomes fortuitously small between the A_3 and A_4 (50 to 60 J·mol^{-1}). Very small energy changes can, therefore, have a disproportionate effect on the extension of these transitions into iron-base systems.

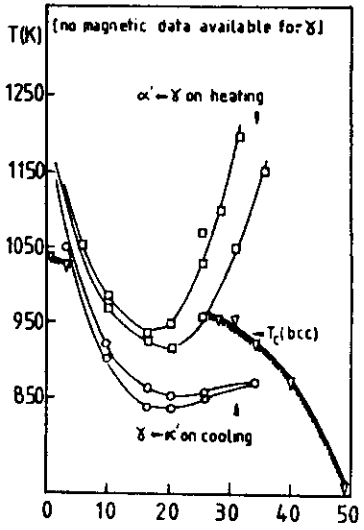
Because of the location of the Curie temperature in pure iron, the effect of magnetic forces on the A_3 is much more pronounced than on the A_4, and various alloying additions produce asymmetrical effects on the two transitions. It is, therefore, not surprising to find a number of unsymmetrical "γ loops" in iron-base systems. A simple division between "γ-loop" formers and "open γ-field" formers is obviously rather naive in these circumstances, and leaves out important variations such as Fe-Co, Fe-Cr, and Fe-Rh, the latter system combining features from the other two diagrams.

The transformation characteristics depicted for Fe-Rh (Fig. 9) and Fe-Co (Fig. 10) do not represent equilibrium situations in the conventional sense. The "phase boundaries" for the α/γ region of the Fe-Rh system plainly refer to a martensitic transformation $\gamma \rightleftarrows \alpha'$, which not only exhibits a high hysteresis, but also shows a markedly different "shape" for the forward and reverse directions. This can be considered as due to a combination of magnetic and chemical ordering factors similar to the effects found in Fe-Pt alloys [17].

The calculated transus lines for the Fe-Co alloys refer to T_0 temperatures, which can, however, be legitimately compared with $(M_s + A_s)/2$ of the Fe-Rh system. The apparently artificial procedure of adding an increment to the free energy of bcc Fe-Co can actually be realized experimentally through the application of an external magnetic field [16, 32]. As well as reproducing some of the characteristics of the Fe-Rh system in this way, Fig. 10 also indicates that the application of a small amount of energy (20 to 25 J·mol^{-1}), such as from an external magnetic field, would cause the phase boundaries to shift sufficiently for a suitable alloy to transform reversibly from 100% austenite to 100% ferrite at 1165 K [32]. This confirms that an external magnetic field must be considered an additional extensive variable just like temperature and pressure. Although the effect of such an external field is normally so small that it can be ignored in the same way as atmospheric pressures for solid state systems, there may be important situations where a phase change is induced by a magnetic field—particularly where superconducting magnets are involved.

With so many magnetic effects occurring in iron-base alloys, one might well ask why cobalt-base alloys, with their much higher Curie temperature, are not prone to similar variations. The answer seems to be that as far as solubility changes of precipitates are concerned the effect is obviously there (compare Fig. 1a, 2, and 1b), but as far as effects on the fcc/cph equilibrium in cobalt-base alloys are concerned, these are not to be expected because the magnetic properties of the two cobalt allotropes are very similar (remember that it is the *relative* magnetic properties that count).

Fig. 9 α/γ Transus in Fe-Rh Alloys



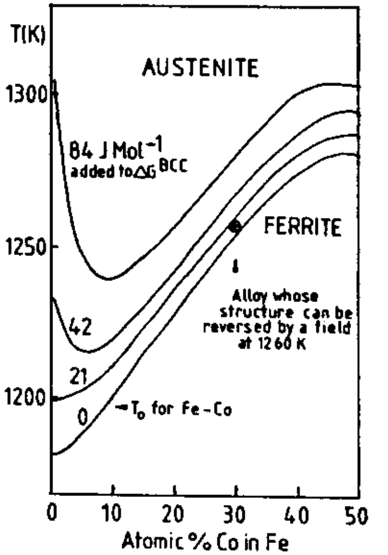
The unusual shape of the α/γ transus in the Fe-Rh system [7] shows features reminiscent of both Fe-Co and Fe-Cr alloys. It is highly likely that this is due to magnetic effects (see Fig. 10).

Effects Associated with Antiferromagnetism

All the effects mentioned so far have been associated with ferromagnetic changes, but similar changes can arise from the presence of antiferromagnetism. Thus, although manganese is well known as a gamma stabilizer, it is also known to favor the formation of an intermediate hexagonal epsilon phase on either deformation or quenching. Gamma iron has an antiferromagnetic transition (Neel temperature) of 80 K, which is raised rapidly by manganese, whereas the magnetic properties of the ϵ phase are hardly affected. The result is that γ is stabilized relative to ϵ in Fe-Mn alloys (Fig. 10) in exactly the same way that γ is stabilized relative to α in Fe-Co alloys (Fig. 8).

In all such instances, whether due to ferro- or antiferromagnetism, these steep transus lines will be accompanied by a very composition-dependent M_s. It can be seen from Fig. 10 that the calculations of the relative stability of γ and ϵ, excluding magnetic factors, predict that ϵ would be the stable phase over an extensive region, contrary to the experimental observation that γ is abruptly stabilized at just below 30% Mn.

Fig. 10 Effect of Decreasing the Free Energy of the α Phase on the Mean α/γ Transus Temperature, T_0 [16]



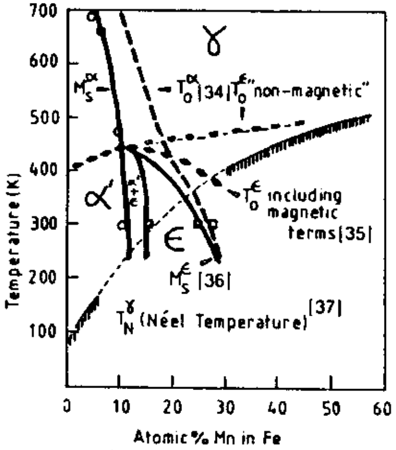
The shape of these curves should be compared to Fig. 9. The magnitude of these changes is well within the general scope of magnetic field contributions.

The pressure dependence of the magnetization can cause significant changes in relative stability and, therefore, in the ratio of γ and ϵ when Fe-Mn alloys are transformed under hydrostatic pressure [33]. Other effects of antiferromagnetism that might be quoted include changes in tetragonality on passing through the Neel temperature; this can result in very complicated phase diagrams, such as exhibited by the Mn-Ni system, but for the purpose of this article must be considered as a secondary factor superimposed on the general features already outlined. (See Fig. 11.)

Interaction of Magnetic and Chemical Ordering

A number of interrelated effects can occur when magnetism interplays with chemical ordering forces. In simple ordering systems, the presence of an AB_3 ordered phase field is accompanied by a corresponding A_3B phase field on the other side of the diagram (e.g., Mg_3Cd and Cd_3Mg). However, in the Fe-Ni system, although there is much experimental evidence for $FeNi_3$, there is no direct confirmation for the existence of Fe_3Ni. Although there are also other factors at work, it is very suggestive that the Curie temperature peaks near $FeNi_3$ in this system and plunges toward zero near Fe_3Ni (Fig. 12) [21, 38]. In $FeNi_3$, magnetic ordering reinforces chemical ordering, because there is a gain in both chemical and magnetic energy when iron and nickel atoms are nearest neighbors to each other.

Fig. 11 Effect of Antiferromagnetism on the γ-ϵ Transition in Fe-Mn Alloys

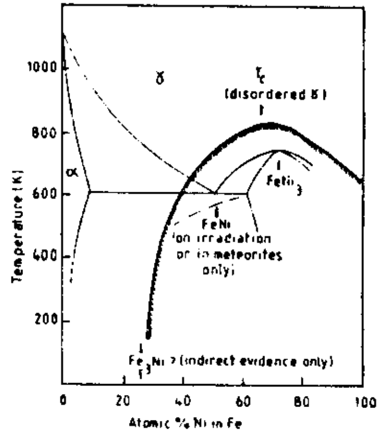


In the absence of the magnetic contribution, the predicted phase equilibria would be completely at variance with experimental results.

Another more subtle interaction between magnetic and chemical ordering is evidenced by the Fe-Al system [19, 20]. Careful investigation has shown the presence of a two-phase region where the two second-order transformations (for magnetic ordering and chemical ordering) intersect (Fig. 13).

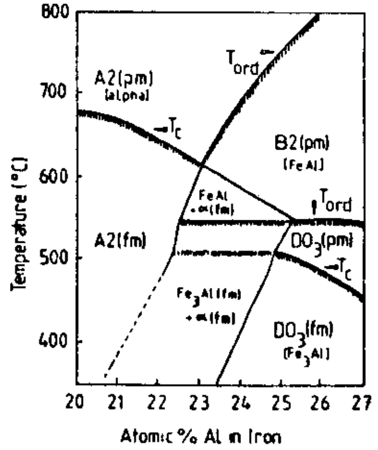
In Fe_3Al, ferromagnetism will not be favored by chemical ordering, because aluminum decreases the Curie temperature sharply and the number of Fe-Fe nearest neighbors is decreased by ordering. This situation favors the alloy splitting up into a mixture of two phases, one iron-rich disordered and ferromagnetic, and the other aluminum-rich, chemically ordered, and with ferromagnetism suppressed to lower temperatures. Both the Fe-Ni system and the Fe-Al system have many additional features, including effects that can be attributed to the existence of antiferromagnetic coupling at certain compositions. In most cases the observed effects, despite their complexity, are generally consistent with quite simple models [39], and it is interesting that the difference between theory and experiment is gradually narrowing as new magnetic models are being developed [18, 23, 39, 40]. For further details, a companion article in this issue should be consulted [41].

Fig. 12 Relation Between Magnetic Ordering and the Existence of Stable Chemically Ordered Superlattices in the Fe-Ni System [38]



The asymmetry between the existence of $FeNi_3$ and the apparent absence of Fe_3Ni is particularly noticeable.

Fig. 13 Partial Equilibrium Diagram for the Fe-Al System



Showing the emergence of two-phase regions where two second-order transformations intersect [19]

Conclusion

There can be little doubt that magnetism plays a key role in the phase equilibria of systems containing magnetic components. Appreciation of this fact has, however, only emerged in relatively recent times, as shown by the dates of the references to this article. This curious fact can be attributed in no small measure to the "β iron" debate, which took place almost 100 years ago and was eventually settled in favor of "β iron being just the paramagnetic form of α iron" [42]. This formulation satisfied the protagonists at the time but completely ignored the fact that a magnetic transformation is energetically as significant as an ordinary phase transformation!

It is a sobering thought that the phrase, "It's just a magnetic transformation", effectively buried the importance of magnetic transformations, together with the demise of β iron, for more than half a century.

Cited References

1. M. Ko and T. Nishizawa, *J. Jpn. Inst. Met.*, *43*, 118 (1979).
2. M. Hasebe and T. Nishizawa, *Calphad*, 4(2), 83 (1980).
3. A. H. Qureshi, *Z. Metallkunde*, *52*, 799 (1961).
4. G. R. Speich, L. Zwell and K. A. Wriedt, *Trans. AIME*, *230*, 939 (1964).
5. M. Ko and T. Nishizawa, *J. Jpn. Inst. Met.*, *43*(2), 126 (1979).
6. H. Kaneko *et al.*, *IEEE Trans.*, *13*, 1325 (1977).
7. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill (1958), plus Elliott (1965) Shunk (1969) supplements.
8. T. Nishizawa, M. Hasebe and M. Ko, *Acta Met.*, *27*, 817 (1979).
9. G. Inden, *Physica*, *103B*, 82 (1981).
10. C. Zener, *Trans. AIME*, *203*, 619 (1955).
11. A. P. Miodownik, *Calphad*, *1*(2), 133 (1977).
12. A. P. Miodownik, Honda Memorial Series, *Invar Alloys*, Chapter 12, Saito, Ed., 228-310 (1978).
13. A. P. Miodownik, Honda Memorial Series, *Invar Alloys*, Chapter 18, Saito, Ed., 429-456 (1978).
14. Y. Nakamura, M. Shiga and S. Santa, *J. Phys. Soc. Jpn.*, *29*, 210 (1969).
15. G. Inden and W. O. Meyer, *Z. Metallkunde*, *66*, 725 (1975).
16. C. T. Peters, Ph. D. thesis, Surrey Univ. (1975).
17. A. P. Miodownik and D. Skinner, International Conference on Martensite Transformations (ICOMAT II), W. Owen, Ed., Cambridge, MA (1979).
18. G. Schlatte and W. Pitsch, *Z. Metallkunde*, *66*, 660 (1975).
19. P. R. Swann, W. R. Duff and R. M. Fisher, *Trans. Met. Soc. AIME*, *245*, 851 (1969).
20. S. M. Allen and J. W. Cahn, *Acta Met.*, *24*, 425 (1976).
21. H. Huthmann, Dr. Nat. Thesis Tech. Hoch., Aachen (1977).
22. C. Wagner, *Acta Met.*, 20, 803 (1972).
23. G. Inden, *Z. Metallkunde*, *68*, 529 (1977).
24. A. P. Miodownik and M. Hillert, *Calphad*, 4(2), 143 (1980).
25. H. Harvig, G. Kirchner and M. Hillert, *Metall. Trans.*, *3*, 329 (1972).
26. A. P. Miodownik, Th. Henig and L. Lucas, Max-Planck Inst., Stuttgart, unpublished (1979).
27. M. G. Stout *et al.*, *Met. Trans.*, *8A*, 1316 (1977).
28. J. L. Meijering, *Philips Res. Rep.*, No. 18, 318 (1963).
29. A. P. Miodownik, *Calphad*, 4(4), 219 (1980).
30. V. Marian, *Ann. Phys.*, 7(11), 459 (1937).
31. R. A. Oriani, *Acta Met.*, *3*, 232 (1955).
32. C. T. Peters and A. P. Miodownik, *Scripta Metallurgica*, *7*, 955 (1973).
33. A. Rabinkin, *Calphad J.*, *3*(2), 77 (1979).
34. J. F. Breedis and L. Kaufman, *Met. Trans.*, 2, 2359 (1971).
35. A. P. Miodownik, Thermodynamics Symposium, Münster Univ., unpublished (1972).
36. A. Holden, J. D. Bolton and E. R. Petty, *J. Iron and Steel Institute* (Sept), 721 (1971).
37. H. H. Ettwig and W. Pepperhoff, *Phys. Stat. Sol.(a)*, *23*(2), 105 (1974).
38. D. Skinner, Ph. D. thesis, Surrey Univ. (1980).
39. G. Inden, *Z. Metallkunde*, *63*, 253 (1972).
40. G. Inden, *Scripta Met.*, *15*, 669 (1981).
41. G. Inden, *Bulletin of Alloy Phase Diagrams*, 2(4), 412 (1982).
42. M. Cohen, Metallography Symposium, AIME, No. 15, 209 (1965).

The Effect of Continuous Transformations on Phase Diagrams

By Gerhard Inden
Max-Planck-Institut für Eisenforschung GmbH
Max-Planck-Strasse 1, D-4000 Düsseldorf

Alloy phase diagrams usually represent the most stable states of alloys at constant pressure in a temperature-versus-composition diagram. The most important information to be taken from such diagrams is whether the stable states are homogeneous or heterogeneous. Phase boundaries subdivide these diagrams into single- and multiphase regions. Transformations from one single-phase state to another generally occur through intermediate heterogeneous multiphase states. However, there are also transformations that may, but need not, occur through heterogeneous equilibria, e.g., atomic and magnetic order-disorder transformations. The dubious character of that kind of transformation has led to an inadequate representation in phase diagrams. The critical temperatures of these transformations are drawn either as broken lines (thus treating them on the same level as unreliable phase boundaries, e.g., Curie temperatures in ferromagnetic systems such as Co-Ni and Fe-Si [1]) or as a pair of broken lines (thereby tacitly presuming heterogeneous equilibria for these transformations, too; e.g., Co-Fe and Fe-Si [1]). It is the aim of this contribution to suggest an appropriate representation of these order-disorder transformations in phase diagrams, the necessity of which becomes conspicuous by the occurrence of unusual heterogeneous phase equilibria.

These unusual phase equilibria are sharply closing miscibility gaps extending either along a critical temperature line of continuous transformations (thus opening and closing at this line) or starting at the critical temperature and opening toward lower temperatures. The temperature/composition point at which the gap sharply closes and from which the critical temperature line continues is called a tricritical point [2]. The conditions for the occurrence of such tricritical points have been discussed in general by Landau [3]. Particular cases for atomic and magnetic ordering have been treated in [4-7] and [8-12], respectively.

For the sake of simplicity, this discussion will be confined to binary alloys. The results, however, remain valid for higher component systems, and the transposition to these situations is straightforward.

General Viewpoints

The phase state of an alloy is defined by its physical properties, such as crystal structure, composition, density, viscosity, etc. If these properties do not only apply to the alloy as a whole but also to every subdivision of it, the state of the alloy is *homogeneous*. The state of the alloy is *heterogeneous* if there are subdivisions of the alloy with differing physical properties. By this definition, any change of physical properties produces a change of the state of the alloy.

Among the infinite variety of states, the equilibrium states at fixed values of the variables -- pressure, temperature, and composition--are of particular interest. Changes of these variables produce transformations of the equilibrium states. It is very useful to attribute a common denomination to all those states that transform continuously into each other: they all belong to the same *phase state* (or simply phase). The discontinuity in the physical properties is, by definition, a prerequisite for the distinction of phases. Heating a crystalline alloy changes its physical properties (e.g., the volume by thermal expansion); however, as long as these changes take place continuously, the contracted state at low temperatures and the expanded state at higher temperatures are not designated as different phases. Consequently, homogeneous states of an alloy must be single-phase states. Heterogeneous states of an alloy with continuously varying physical properties, e.g., produced by a concentration gradient, are single-phase states. Heterogeneous states with discontinuously varying properties are multiphase states, and each subdivision of the alloy exhibiting homogeneous properties is usually identified with the corresponding phase.

The physical properties of an alloy can be expressed as derivatives of the molar Gibbs energy,* G: e.g., entropy, $S = -\frac{\partial G}{\partial T}|_p$; volume, $V = \frac{\partial G}{\partial p}|_T$; or specific heat capacity, $c_p = -\frac{\partial^2 G}{\partial T^2}|_p$. This immediately suggests classification of the phase transformations according to Ehrenfest's scheme [13]: a transformation is of nth order if G and its $(n-1)$-order derivatives are continuous and the nth order derivatives change discontinuously at the transformation. A typical second-order transformation would, thus, produce a finite jump of c_p at the transformation.

Model calculations of atomic (bcc, [4, 5]; fcc, [6, 7]) and magnetic [12, 14] order-disorder transformations in alloys predict first- and second-order transformations. In real systems, however, it seems to be accepted that c_p does not take finite values at the transformation. At least for magnetic transformations, this effect has been established experimentally (see [15]). At the Curie temperature, c_p shows a logarithmic singularity. The same behavior can be expected for atomic ordering reactions at the critical temperature of long-range order. In these instances, it is more difficult to decide by experiments whether or not c_p takes finite values at the critical temperature. Ordering reactions are diffusion controlled, and it is difficult to ascertain that equilibrium states are in fact established during the c_p measurements. However, a rise of c_p to infinity for atomic ordering reactions at the critical temperature has been found most recently by Monte Carlo simulations [16]. These "computer experiments" come closest to an ideal experiment. Consequently, Ehrenfest's classification is not applicable to the most general order-disorder transformations, and one should have recourse to a more general classification, such as the one proposed by Tisza [17, 18].

Fortunately, it is not necessary to distinguish second-order from higher-order transformations in phase diagram calculations and representations, because they all produce qualitatively similar contributions to the Gibbs energy. Therefore, it is often sufficient to classify the transformations into *discontinuous* (first-order) and *continuous* (second- or higher-order) *phase transformations*, the continuity or discontinuity being associated only with the physical properties that derive from G by first-order derivatives.

Phase Transformations Under Constraint of Homogeneity. Before considering heterogeneous equilibria, it is very helpful to consider first the equilibria under the constraint of homogeneity. In this instance, each state can be associated with a single phase. The temperature vs. composition diagram indicating the ranges where a given phase is the equilibrium state is called the *configuration diagram*. Different single-phase regions are separated by transformation lines which should be drawn as solid lines for first-order transformations and hatched lines** for higher-order transformations (see Fig. 2).

At first, atomic ordering in a binary alloy $A_{1-x}B_x$ should be considered. The state of order is defined by two different sets of parameters.

- The short-range order (sro) parameters $p_{AB}^{(k)}$, which are defined as the ratio of A-B bonds between k-th neighbors to the total amount of bonds in the alloy, $p_{AB}^{(k)} = \frac{N_{AB}^{(k)}}{\frac{1}{2}z^{(k)}N_L}$,*** where $z^{(k)}$ is the coordination number of the k-th shell and N_L is Avogadro's number (1 mole of alloy).
- The long-range order (lro) parameters p_B^L, which describe the lro by means of the fraction p_B^L of B-atoms on appropriately chosen sublattices, L (see, e.g., [4] and Fig. 1 for bcc and [6] for fcc lattices).

With constant pressure, the equilibrium states minimize Gibbs energy. Because we also maintain the composition

---

*In this article, all thermodynamic entities will be considered for 1 mole of substance. Therefore, it is not necessary to introduce a special notation for these quantities.

**A hachure for indicating higher-order transformations was first suggested by Swann, Duff, and Fisher in their TEM-work on the ordering in Fe-Al alloys [19].

***$p_{AB}^{(k)}$ takes the value $2x(1-x)$ in the random alloy. Instead of $p_{AB}^{(k)}$, the isotropic "Cowley-Warren short range order parameters" α_k often are introduced. They are defined as the deviation from the random state $p_{AB}^{(k)} = 2x(1-x)(1-\alpha_k)$.

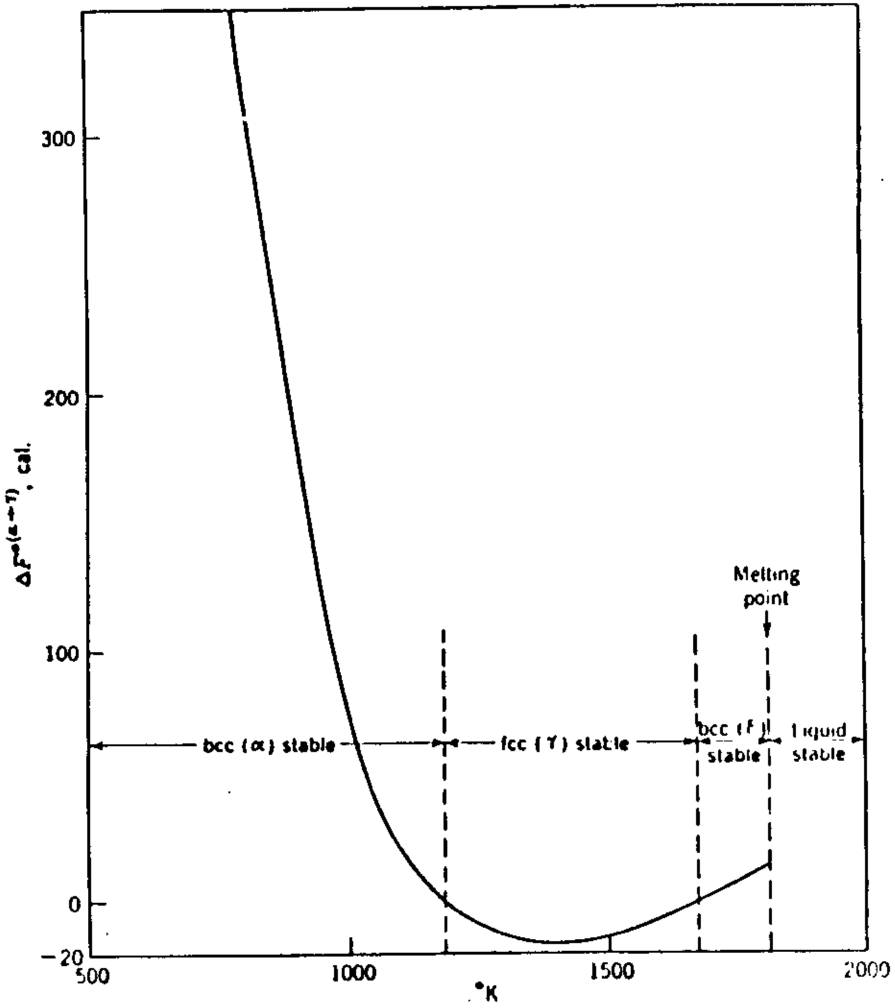


FIG. 16-1. The free-energy change accompanying the transformation of pure bcc to fcc iron.

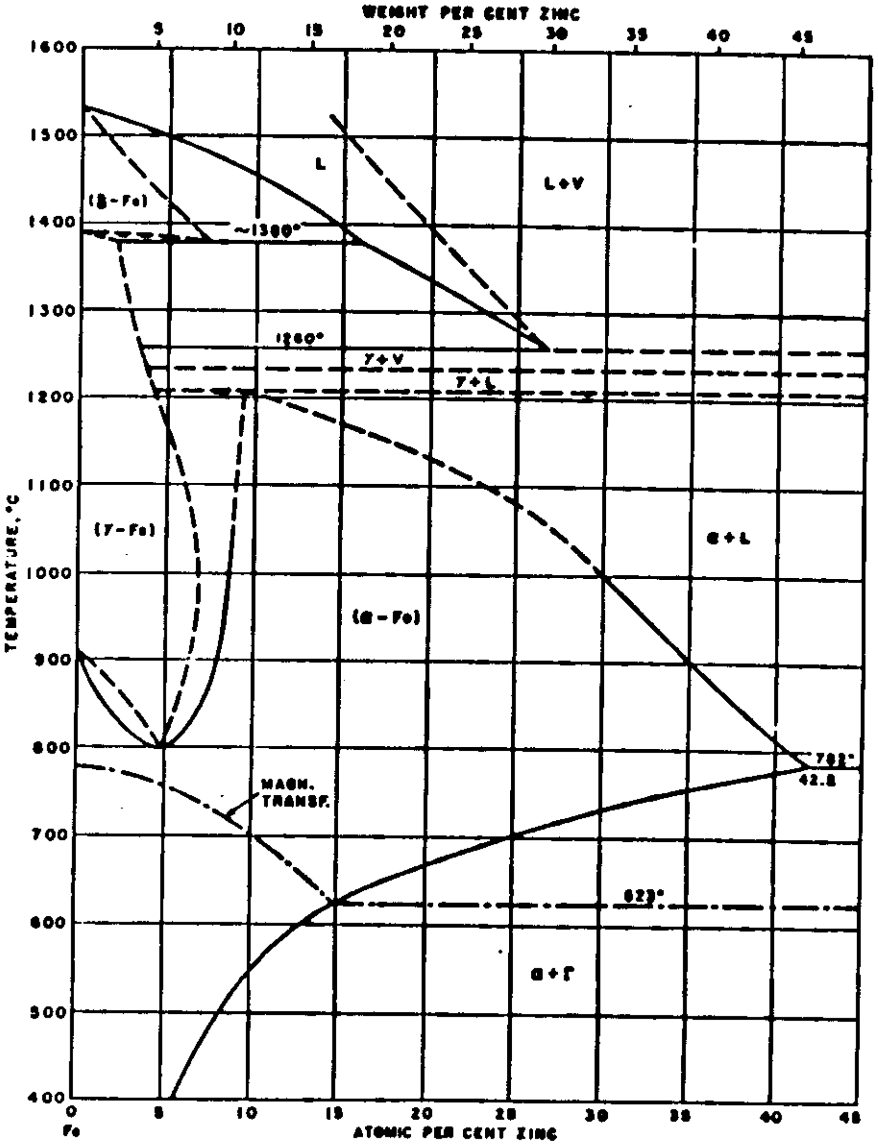
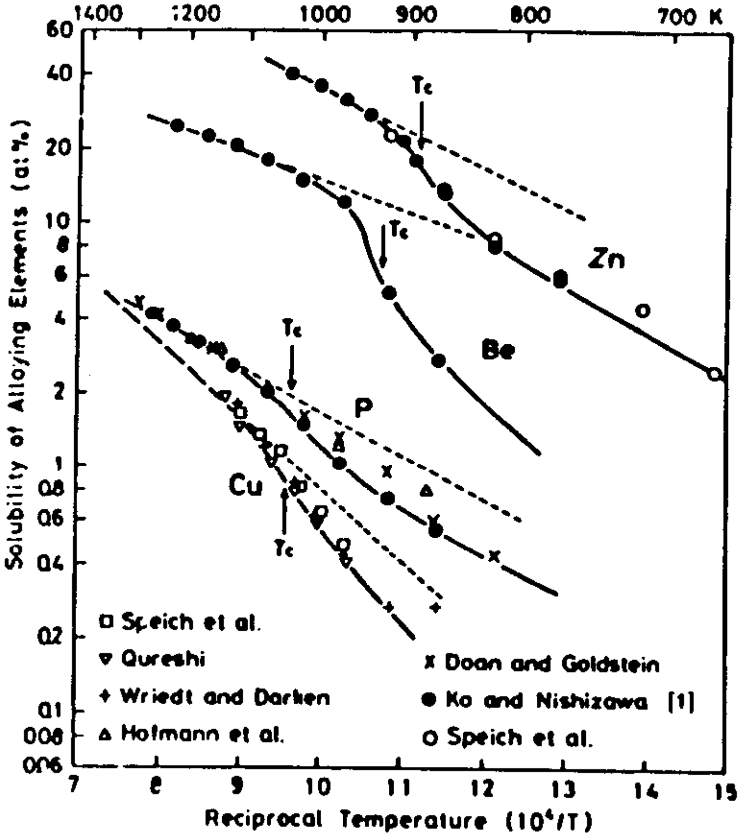
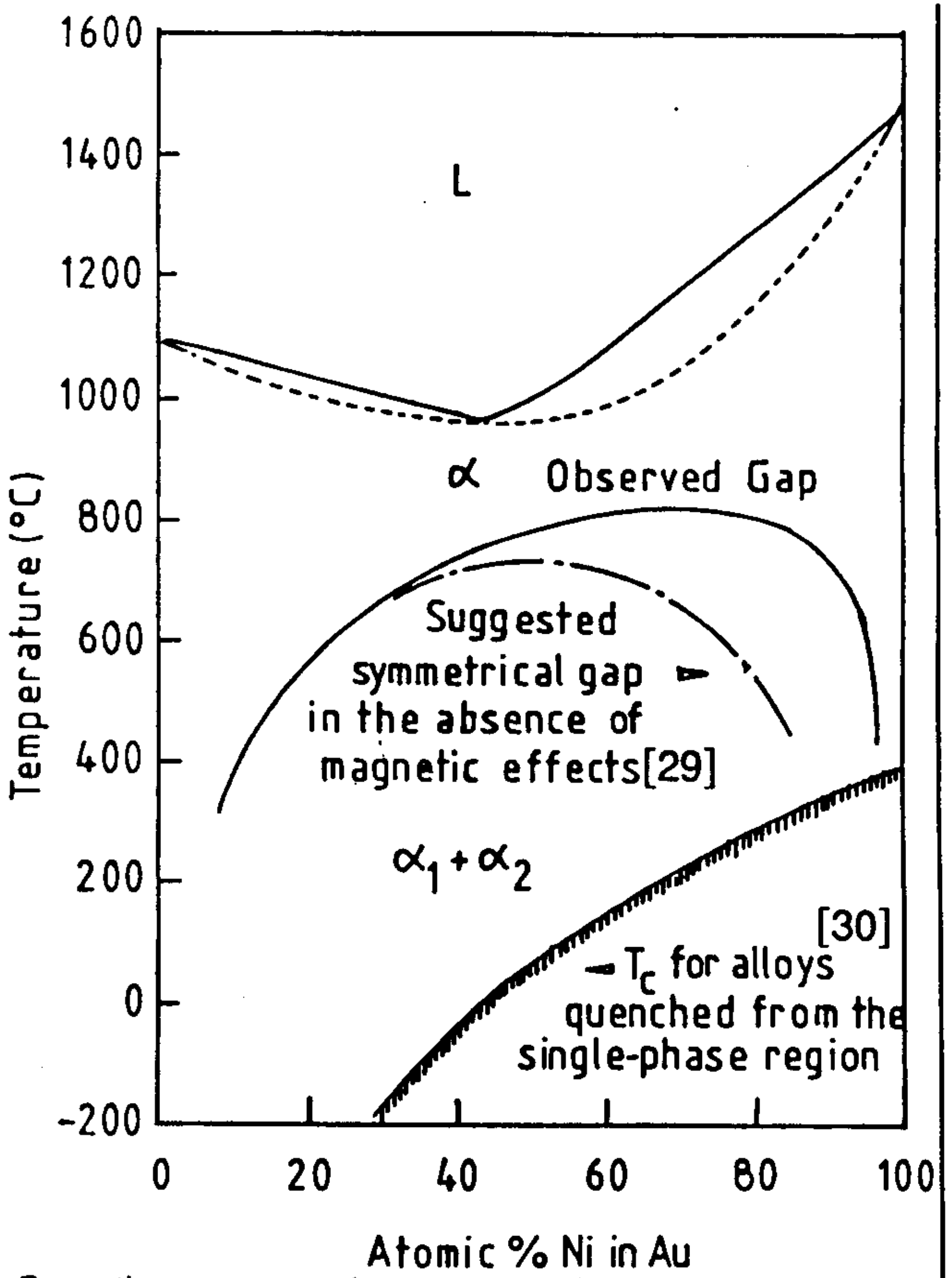


Fig. 232. Fe-Zn



(a) bcc iron [8]



Few other property changes can arise so suddenly in the middle of an alloy system that does not exhibit compound formation.

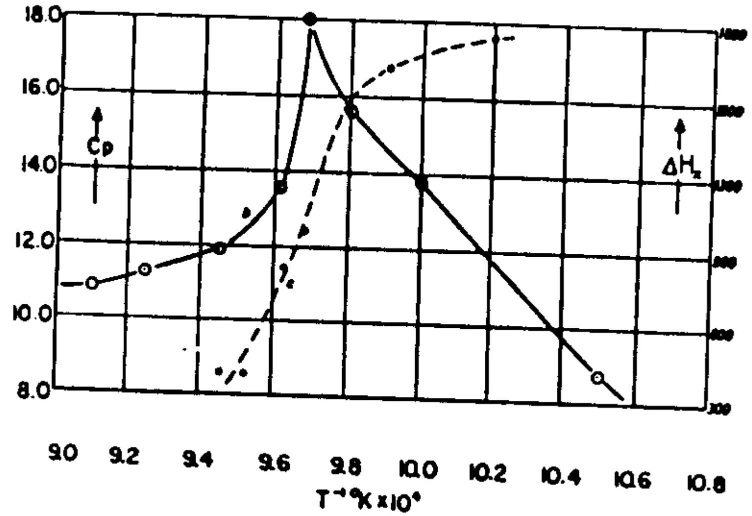


Fig. 4—A comparison of the heat capacity anomaly in the Curie point region (curve *b*) with the ratio of the measured diffusivity to the diffusivity extrapolated from the high temperature line (curve *a*). The excess enthalpy (curve *c*) is also given for comparison.

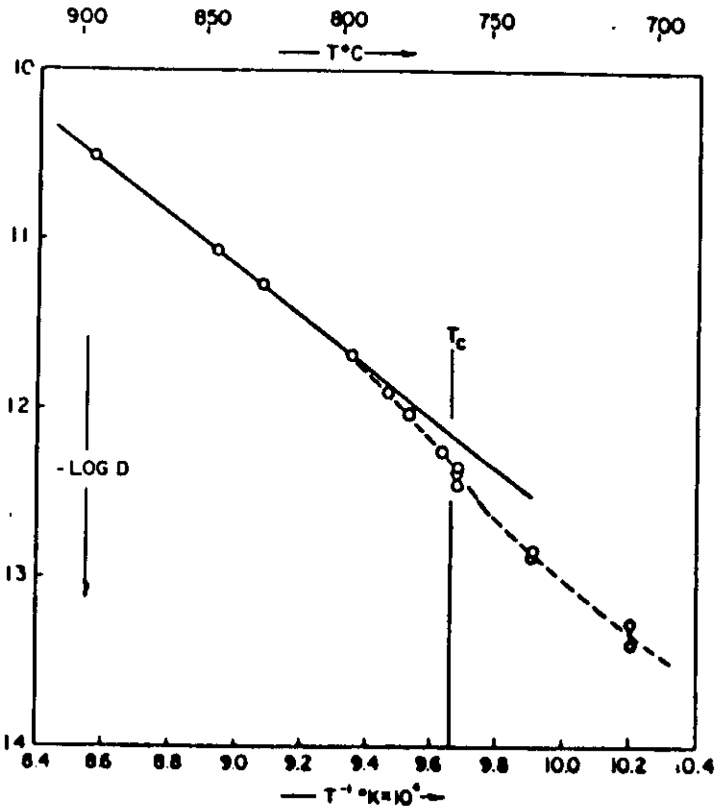


Fig. 3—The experimental results of this investigation showing their relation to the Curie temperature for ferromagnetism.

#1

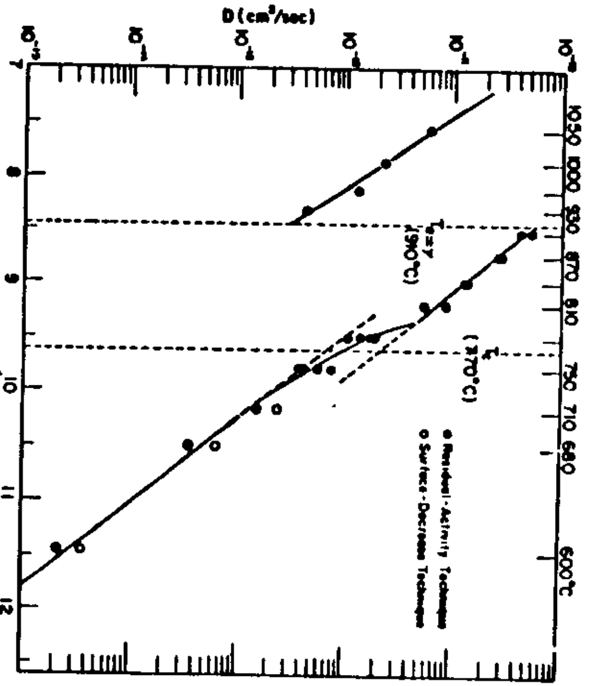
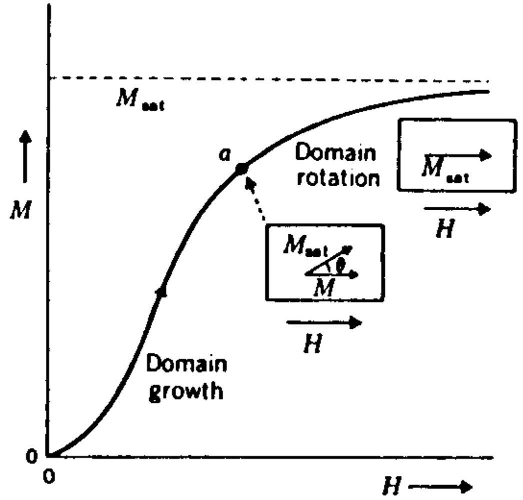
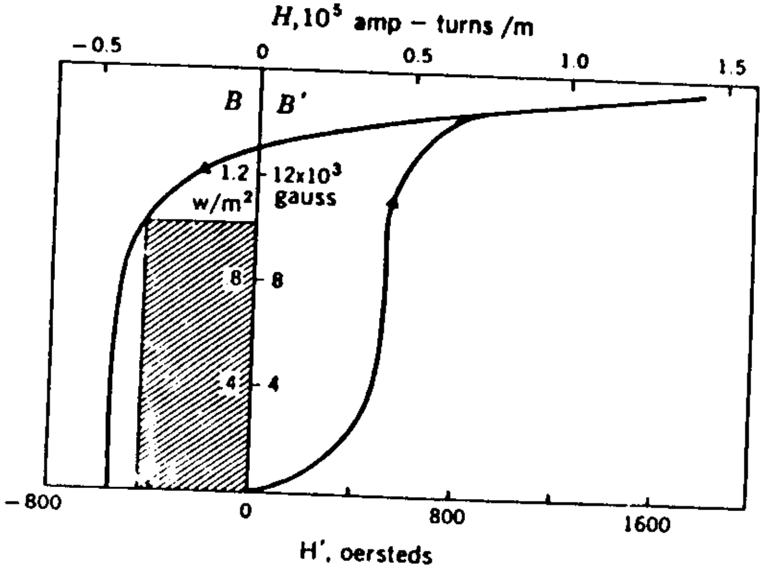


Fig. 3. Temperature dependence of diffusion coefficient of nickel into iron.

#2





#3

Table 20-1 Properties of typical soft magnetic materials

Material	Chemical composition	M_{sat} 10^5 amp-turns/m	μ_r(max)	ρ, ohm$_{-m}$	Hysteresis loss, joules/ Kg/cycle
Fe	Nominally pure	17.5	5,000	10×10^{-8}	0.03
Fe-2%Si	Fe-2%Si	16.7	7,500	35×10^{-8}	0.02
G.O. Si-Fe	Fe+4%Si	15.5	30,000	55×10^{-8}	0.005
Hipernik	Fe+50%Ni	12.7	60,000	45×10^{-8}	0.003
78-Permalloy	Fe+ 78%Ni	8.7	100,000	16×10^{-8}	0.0005
Supermalloy	Fe+5%Mo+79%Ni	7	1,000,000	60×10^{-9}	0.0001
Mn-Zn ferrite	$Mn_{1/2}Zn_{1/2}Fe_2O_4$	3	2,500	20×10^{-2}	0.001
Metglas 2605 SC	$Fe_{81}B_{13.5}Si_{3.5}C_2$	12.7	300,000	125×10^{-8}	0.004
6010	$Co_{58}Ni_{10}Fe_5Si_{11}B_{16}$	4.0	600,000	130×10^{-8}	0.004

#4

Table 20-2 Approximate magnetic characteristics of typical permanent-magnet materials

Name	Year introduced	Composition	H_c, amps-turns/m	B_r, webers/m^2	$(BH)_{max}$, joules/m^3	$(BH)_{max}$, GOe
Fe			75	1.5	100	12,500
Tungsten steel	1885	6%W, 1%C, 93%Fe	5,000	1.0	3,000	375,000
K.S. steel	1917	35%Co, 7%W, 2%Cr, 0.6%C, bal. Fe	10,000	1.0	7,000	875,000
Remalloy	1931	12TCo, 17%Mo, 71%Fe	20,000	1.0	12,000	1.25M
Alnico II	1934	12%Co, 17%Ni, 10%Al, 6%Cu, 55%Fe	50,000	0.7	17,000	2.1
Alnico V	1940	24%Co, 14%Ni, 8%Al, 3%Cu, 51%Fe	50,000	1.2	45,000	5.6
Indox I	1954	$BaFe_{12}O_{19}$	140,000	0.22	8,000	1.0
Indox V	1956	$BaFe_{12}O_{19}$(oriented)	160,000	0.38	28,000	3.5
Co-Rare earth	1970's	$Co_{3.5}Cu_1Fe_{.5}Sm$	480,000	0.7	80,000	10
Mixed-Co-RE Heat-treated	1970's				160,000	20
Fe-base-RE-B	1985	$Nd_2Fe_{14}B$	900,000	1.2	300,000	39

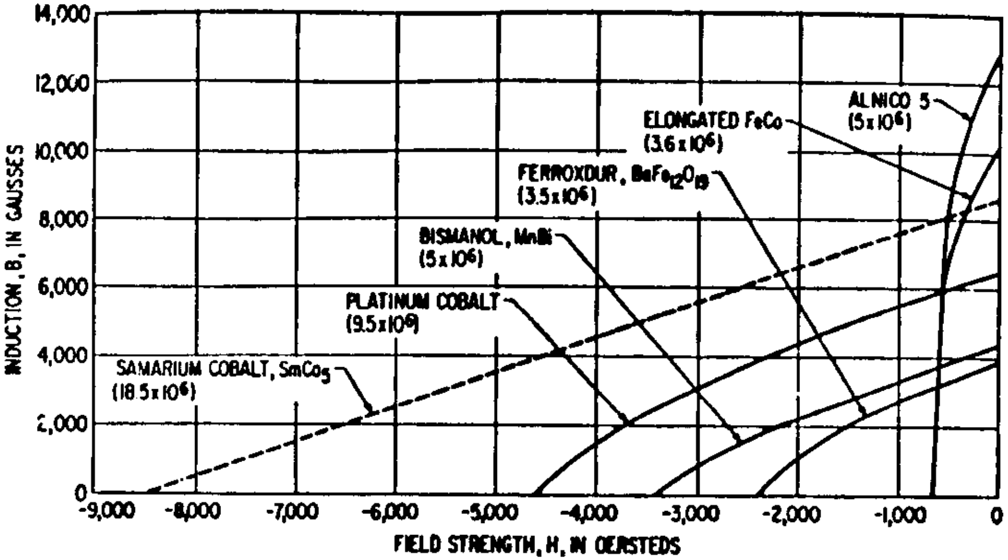


FIG. 5f-12. Demagnetization curves and maximum energy products, $(BH)_m$, of several types of permanent-magnet materials. (*Prepared by H. H. Helms and E. Adams, U.S. Naval Ordnance Laboratory.*)

International Council on Alloy Phase Diagrams

Prof. H. I. Aaronson
Carnegie-Mellon University, USA

Dr. F. Aldinger
W. C. Heraeus GmbH, F R Ger

Dr. T. R. Anantharaman
Banaras Hindu University,
India

Dr. I. Ansara
Domaine Universitaire, France

Dr. D. P. Antia
Industrial and Management
Consultant, India

Mr. H. Baker
American Society for Metals, USA

Dr. L. H. Bennett
National Bureau of Standards, USA

Dr. C. Bernard
Domaine Universitaire, France

Prof. L. Brewer
University of California-Berkeley,
USA

Mr. K. J. Brondyke
Aluminum Company of America,
USA

Dr. J. Cahn
National Bureau of Standards, USA

Dr. G. C. Carter
National Academy of Science, USA

Mr. P. J. Cascone
J. F. Jelenco & Co., USA

Prof. Y. A. Chang
University of Wisconsin—Madison,
USA

Prof. J. W. Christian
University of Oxford, UK

Prof. M. Cohen
Massachusetts Institute of
Technology, USA

Dr. J. R. Cuthill
National Bureau of Standards, USA

Dr. R. F. Decker
Inco Limited, USA

Prof. J. F. Elliott
Massachusetts Institute of
Technology, USA

Prof. R. P. Elliott
Cleveland State University, USA

Dr. E. Epremian
National Research Council, USA

Prof. P. Feschotte
Université de Lausanne, Switz

Dr. N. A. Gokcen
U. S. Bureau of Mines, USA

Dr. A. G. Gray
American Society for Metals, USA

Prof. K. A. Gschneidner, Jr.
Iowa State University, USA

Dr. A. J. Heckler
Armco Inc., USA

Prof. M. Hillert
Royal Institute of Technology,
Sweden

Dr. F. Holtzberg
IBM Corporation, USA

Prof. J. J. Hren
University of Florida, USA

Dr. R. I. Jaffee
Fossil Fuel & Advanced Electric
Power Research Institute, USA

Dr. L. Kaufman
ManLabs Inc., USA

Mr. H. D. Kessler
Cabot Corporation, USA

Dr. G. Kirchner
Metallwerk Berndorf, Austria

Dr. J. Kittl
Comision National de
Energia Atomica, Argentina

Dr. H. J. Klein
Cabot Corporation, USA

Prof. O. J. Kleppa
University of Chicago, USA

Prof. O. Kubaschewski
Rheinisch-Westfälische
Technischen Hochschule
Aachen, F R Ger

Mr. E. L. Langer
American Society for Metals, USA

Dr. R. A. Laudise
Bell Laboratories, USA

Dr. J. D. Livingston
General Electric Co., USA

Mr. W. S. Lyman
Copper Development Assn., Inc.,
USA

Dr. D. J. McPherson
Kaiser Aluminum & Chemical
Corp., USA

Dr. C. L. Magee
Ford Motor Co., USA

Prof. T. B. Massalski
Carnegie-Mellon University, USA

Dr. R. Mehrabian
National Bureau of Standards, USA

Dr. W. G. Moffatt
General Electric Co., USA

Dr. C. H. Moore
International Copper Research
Assn., USA

Dr. Z. Moser
Institute for Metals Research,
Poland

Prof. J. Muller
Université de Genéve, Switz

Prof. J. P. Nielsen
International Precious Metals
Institute, USA

Prof. T. Nishizawa
Tohoku University, Japan

Prof. J. Nutting
Leeds University, UK

Prof. A. Palenzona
University of Genoa, Italy

Dr. J. M. Parks
Lincoln Electric Co., USA

Dr. P. A. Parrish
U. S. Army Research Office, USA

Dr. H. W. Paxton
U. S. Steel Corp., USA

Prof. W. B. Pearson
University of Waterloo, Canada

Prof. A. Pelton
University of Montreal, Canada

Prof. G. Petzow
Max-Planck-Institut für
Metallforschung, F R Ger

Dr. R. K. Pitler
Allegheny Ludlum Steel Corp., USA

Mr. A. Prince
Hirst Research Centre
General Electric Co., Ltd., UK

Dr. S. F. Radtke
International Lead Zinc Research, USA

Mr. P. W. Ramsey
A. O. Smith Corp., USA

Prof. G. V. Raynor
University of Birmingham, UK

Dr. R. J. Reynik
National Science Foundation, USA

Prof. F. N. Rhines
University of Florida, USA

Mr. G. H. Robinson
General Motors Research
Laboratories, USA

Dr. W. P. Roe
ASARCO Inc., USA

Prof. M. Rosen
Ben Gurion University, Israel

Prof. W. Rostoker
University of Illinois—Chicago
Circle, USA

Dr. E. I. Salkovitz
Office of Naval Research, USA

Prof. E. M. Savitsky
Academy of Sciences, USSR

Mr. A. O. Schaefer
The Metal Properties Council, Inc., USA

Dr. L. McD. Schetky
International Copper Research
Assn., USA

Dr. E. A. Schoefer
Metallurgical Consultant, USA

Dr. M. Semchyshen
Climax Molybdenum Co., USA

Dr. I. S. Servi
Metallurgical Consultant, USA

Prof. S. Sōmiya
Research Laboratory of
Engineering Materials, Japan

Prof. C. Souleau
University de Paris, France

Dr. P. J. Spencer
Rheinisch-Westfälische
Technischen Hochschule
Aachen, F R Ger

Prof. R. W. Staehle
University of Minnesota, USA

Prof. Q. -L. Ten
Ministry of Metallurgical Industries,
P R China

Mr. F. L. VerSnyder
United Technologies Research
Center, USA

Dr. R. M. Waterstrat
National Bureau of Standards, USA

Prof. C. A. Wert
University of Illinois, USA

Dr. J. H. Westbrook
General Electric Co., USA

Prof. J. C. Williams
Carnegie-Mellon University, USA

Committee on Constitution of Binary Alloys

Prof. T. B. Massalski, Chairman
Carnegie-Mellon University, USA

Dr. I. N. Ansara
Domaine Universitaire, France

Mr. H. Baker
American Society for Metals, USA

Dr. L. H. Bennett
National Bureau of Standards, USA

Prof. L. Brewer
University of California-Berkeley,
USA

Dr. J. Cahn
National Bureau of Standards, USA

Dr. J. Cuthill
National Bureau of Standards, USA

Dr. R. P. Elliott
Cleveland State University, USA

Dr. K. A. Gschneidner, Jr.
Iowa State University, USA

Prof. M. Hillert
Royal Institute of Technology,
Sweden

Dr. O. Kubaschewski
Reinisch-Westfälische
Technischen Hochschule
Aachen, F R Ger

Prof. J. Nutting
Leeds University, UK

Dr. W. B. Pearson
University of Waterloo, Canada

Prof. A. D. Pelton
University of Montreal, Canada

Prof. J. H. Perepezko
University of Wisconsin-Madison
USA

Mr. A. Prince
General Electric Co., Ltd., UK

Prof. F. N. Rhines
University of Florida, USA

Dr. I. S. Servi
Consultant, USA

Dr. R. M. Waterstrat
National Bureau of Standards, USA

Dr. J. H. Westbrook
General Electric Co., USA

Committee on Constitution of Higher-Order Alloys

Mr. A. Prince, Chairman
General Electric Co., Ltd., UK

Dr. J. D. Livingston, Vice
Chairman
General Electric Co., USA

Dr. F. Aldinger
W. C. Heraeus GmbH, F R Ger

Dr. I. N. Ansara
Domaine Universitaire, France

Mr. H. Baker
American Society for Metals, USA

Prof. L. Brewer
University of California-Berkeley,
USA

Mr. P. J. Cascone
J. F. Jelenco & Co., USA

Dr. Y. A. Chang
University of Wisconsin-Madison
USA

Dr. J. R. Cuthill
National Bureau of Standards, USA

Dr. J. F. Elliott
Massachusetts Institute of
Technology, USA

Dr. E. -Th. Henig
Max-Planck-Institut fur
Metallforschung, F R Ger

Prof. M. Hillert
Royal Institute of Technology,
Sweden

Dr. L. Kaufman
ManLabs, Inc., USA

Dr. O. Kubaschewski
Rheinisch-Westfälische
Technischen Hochschule
Aachen, F R Ger

Dr. R. A. Laudise
Bell Laboratories, USA

Prof. T. B. Massalski
Carnegie-Mellon University, USA

Prof. A. Pelton
University of Montreal, Canada

Dr. G. Petzow
Max-Planck-Institut fur
Metallforschung, F R Ger

Prof. G. V. Raynor
University of Birmingham, UK

Prof. F. N. Rhines
University of Florida, USA

Prof. C. Souleau
University de Paris Sud XI,
France

International Committee on
Phase Diagrams

~ 100 Members world-wide

Chairmen: 1. Larry Bennett NBS
2. Hugh Baker ASM

Binary diagram coordinator:
T. Massalski Carnegie-Mellon U.

Purpose: 1. Coordinate collection of phase diagrams.
2. Assemble thermodynamic data on alloys.
3. Publish a journal.
4. Publish collections of diagrams.
5. Computerize diagrams.

HOW ARE ALLOYS STRENGTHENED?

1. Modes of deformation.
   Dislocations   Grain boundary slip
   Twinning   Vacancy motion
2. Mechanisms of strengthening.
   Work hardening
   almost all alloys
   Solid solutions   brass, stainless steels
   Precipitates   Al, Steels, bcc metals
   Spinodal decomposition
   Composites   Can increase E as well as Y.S.
   Martensites   (Steels and Shape-memory Alloys)

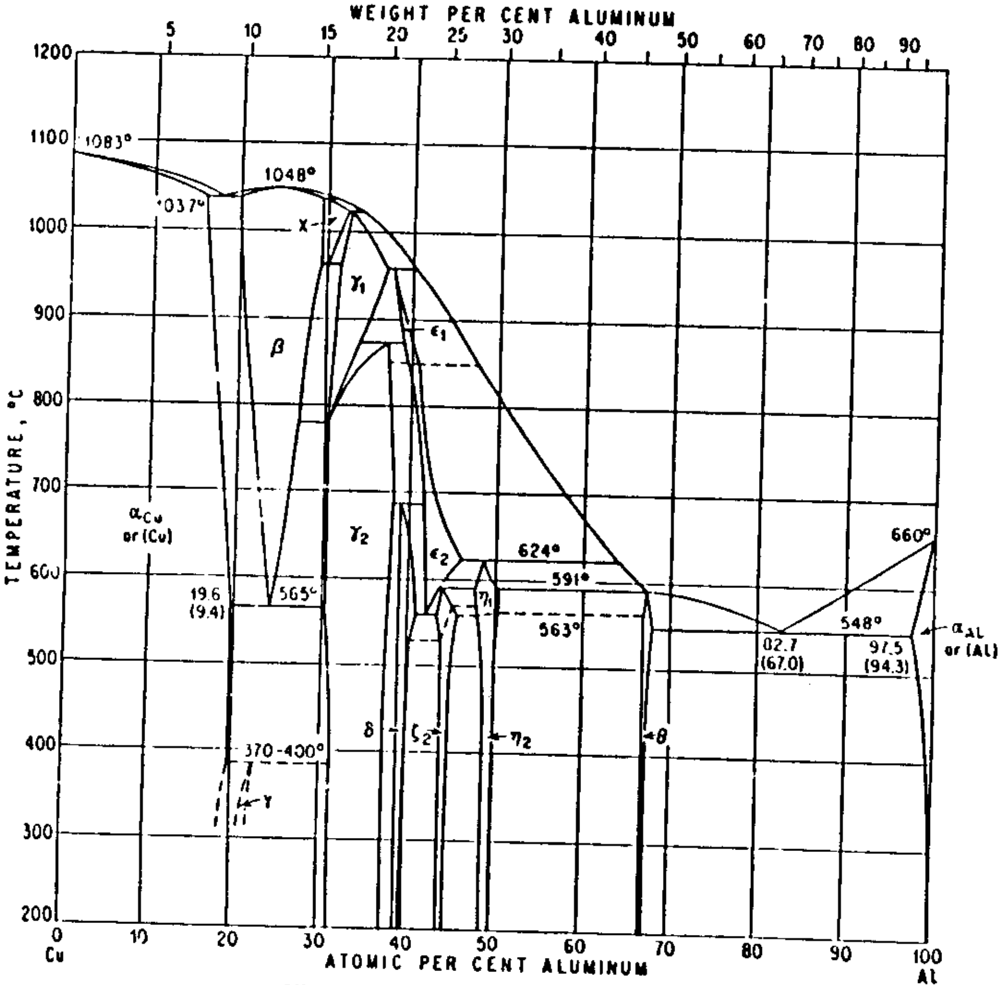


Fig. 52. Al-Cu. (See also Fig. 53.)

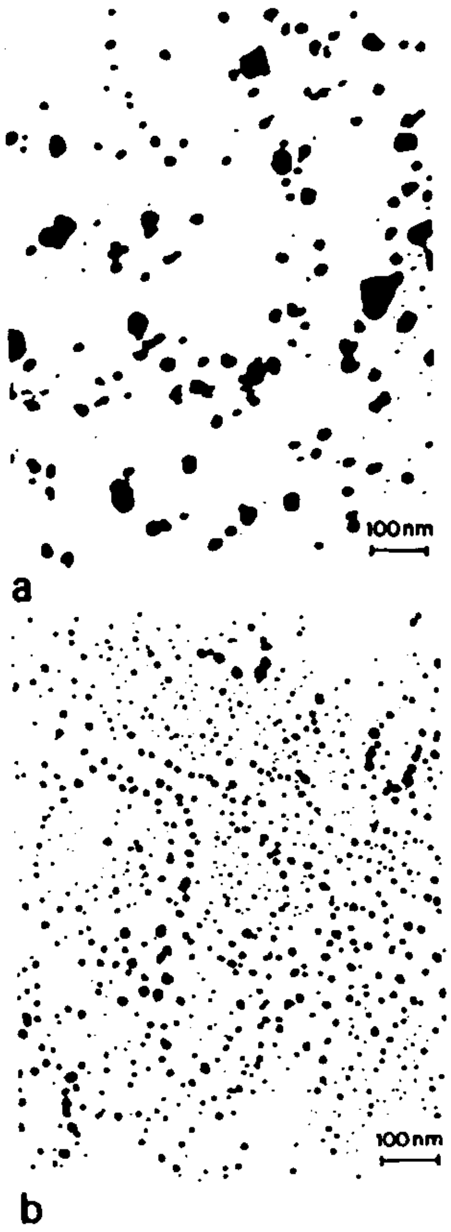


Fig 5 Precipitation distribution in the Al alloy containing 5.2% Cu after aging for a — 3000 min at 90°C; b — 30 min at 90°C with a dynamic stress amplitude of 180 MPa

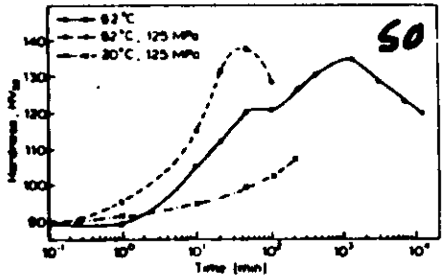


Fig. 1 Hardening curves for Al alloy containing 3.8% Cu

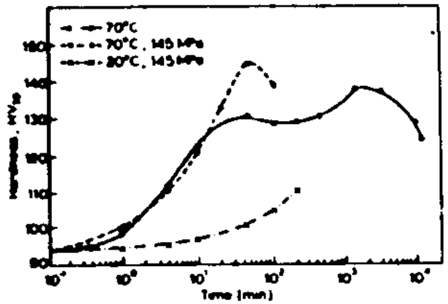


Fig. 2 Hardening curves for Al alloy containing 4.1% Cu

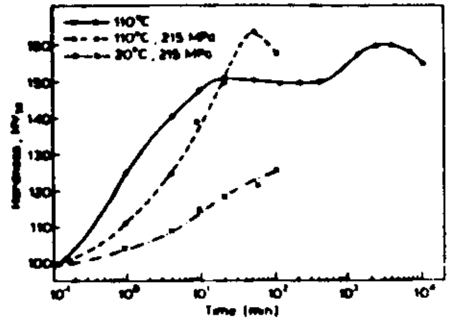


Fig. 3 Hardening curves for Al alloy containing 5.2% Cu

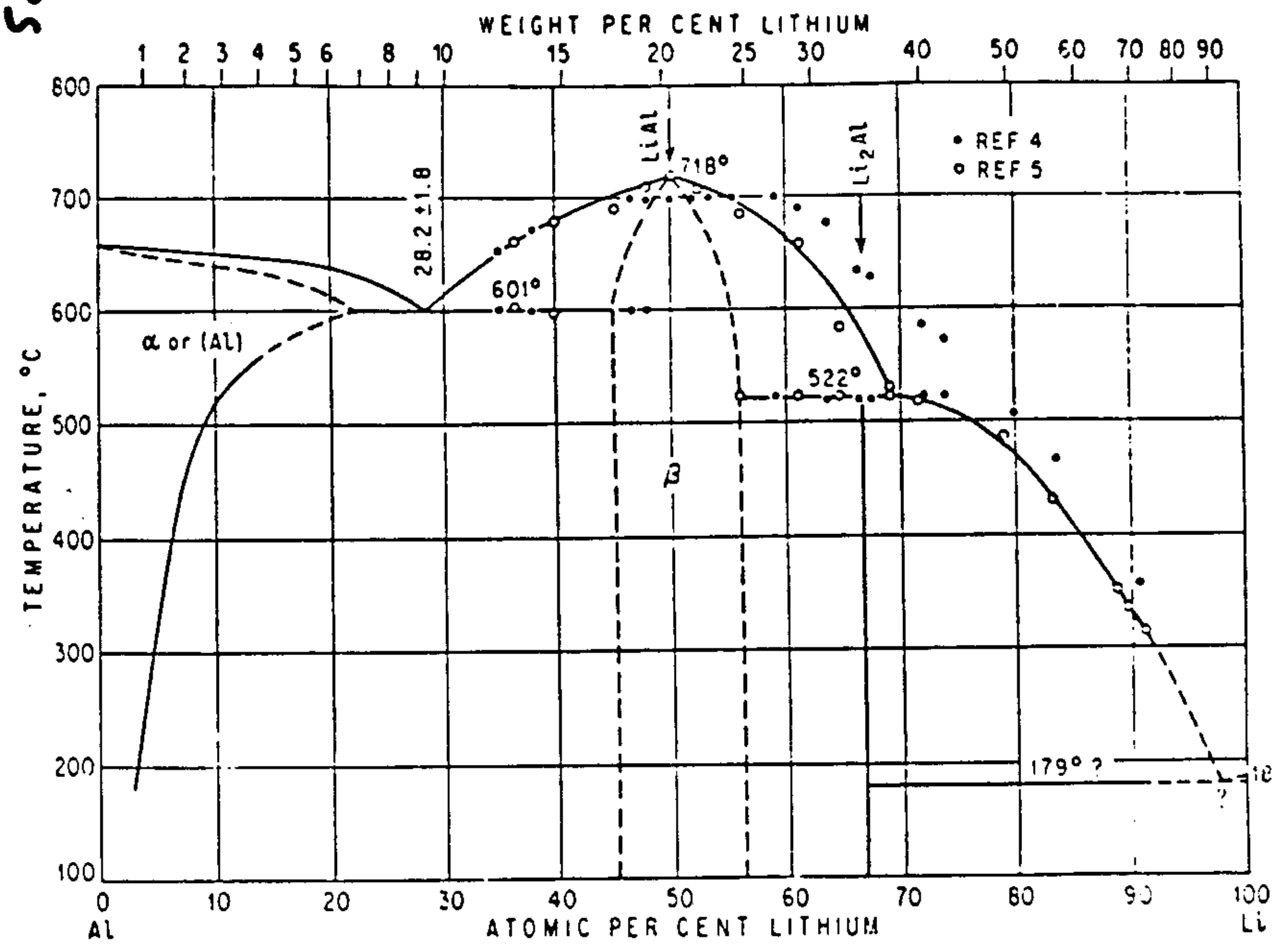


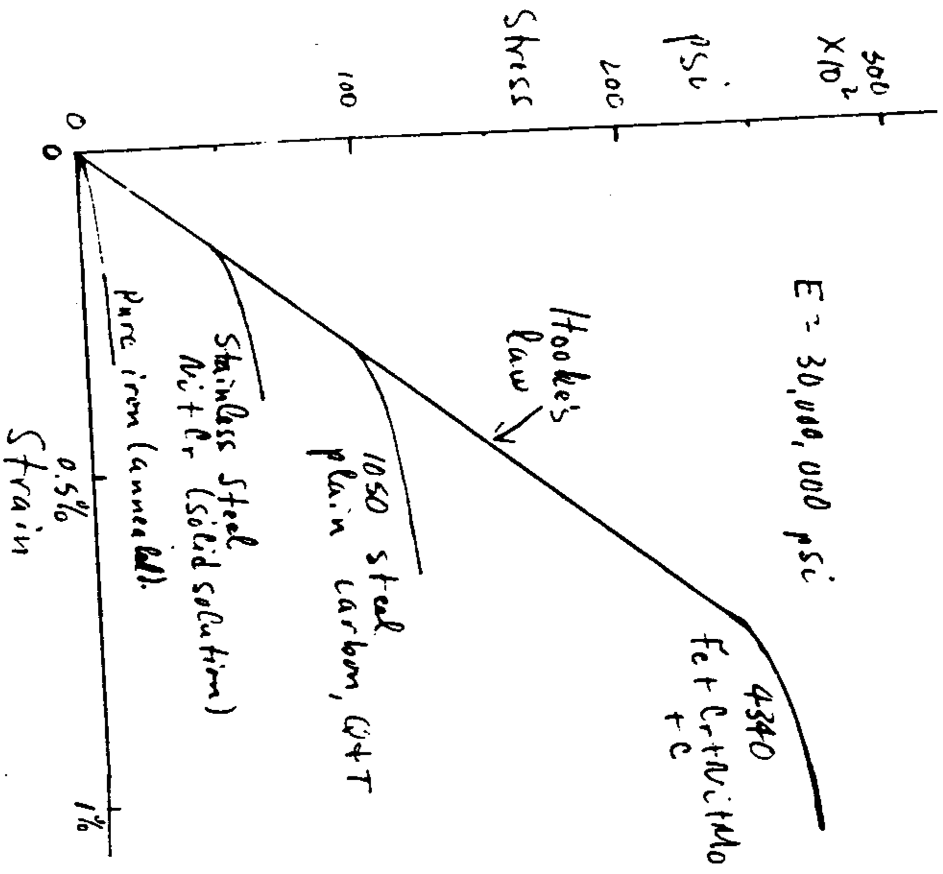
Fig. 63. Al-Li. (See Note Added in Proof.)

ENRICO FERMI: Spend your mornings on simple physical measurements: specific heats, electrical properties, elastic constants, half lives of decay,........

Spend your afternoons working on problems of "Nobel Prize" quality: Theories of atomic structure, forces in the nucleus, grand theories of the nature of magnetism,.......

THE SURPRISING THING IS THIS:

You never know whether the Prize will come from what you do in the MORNING or what you do in the AFTERNOON!



SHAPE-MEMORY ALLOYS

1. Undergo deformation by twinning.
   Strain can be very large. >1%
2. Can exert high stress. >100 kpsi
3. Can "remember" geometry at other
   temperatures.
4. Reversible millions of times.
5. Alloys: AuCd, TiNi, CuZn,------

56

FROTECTIVE MECHANISM

1. During Infiltration Frotective Layer Forms.
   Intermetallic alloy of Cu-Fe-Co.
2. Shields Iron so that it does not dissolve
   in molten Copper.
3. After some time, Cobalt diffuses into
   Iron and protective layer disappears.
4. Frotection disappears.

55

LIQUID METAL INFILTRATION OF SINTERED POWDERS

1. Fills pores. Gives parts of higher density.
2. Fills cracks which lead to fracture.
3. Copper in sintered iron is a good application.
   Strengthens alloy. Improves fracture resistance.
   Increases fatigue resistance.
   Absorbs acoustic energy: Gives QUIET-RUNNING gears.
4. BUT: One large metallurgical problem.
   Iron DISINTEGRATES if exposed to Cu too long.
   CORRECTIVE PROCEDURE: Add a bit of COBALT to copper.
   Keep infiltration time SHORT.
   QUESTION: Why does Co improve the product?

Summary

1. Physics is fun!!
2. Many applications yet exist in Materials Science.
3. Many important problems can still be done by individuals -- you do not need $1 M budgets.

   But you do need to be perceptive.
4. Take advantage of every opportunity to meet with other scientists and with technologists.

Today's Columns

Metal alloys that can dramatically change shape with variations in temperature are welcomed by scientists. A square inch of one particular alloy expands with such strength that it can move a 50,000-pound object, Technology. [29.]

THE NEW YORK TIMES, THURSDAY, DECEMBER 26, 1985

Technology

Stuart Diamond

A Phenomenon In Metallurgy

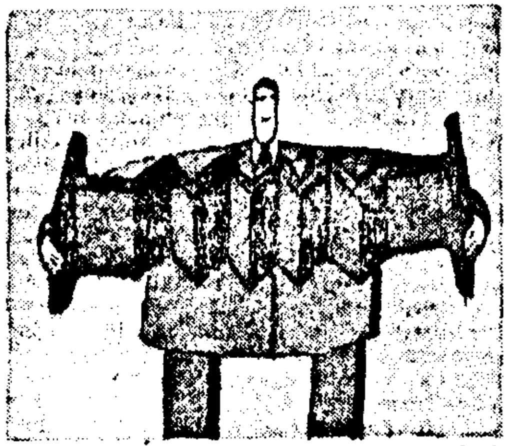
IT looks like an ordinary brass spring. But when dropped into a cup of boiling water, it instantly uncoils to five times its length, pinning itself against the cup's walls. When the water is poured out, the spring responds to the cooler air by instantly recoiling to its original shape.

This phenomenon, called "shape memory," typifies what some engineers call one of the most exciting metallurgy advances in decades. Scientists have found a host of metal alloys that can dramatically change shape based on temperature.

The force of the change can be enormous. A square inch of one alloy, for example, expands with such strength that it can move a 50,000-pound object. The applications are many: opening and closing windows, replacing moving parts in engines, serving as muscles in robot hands. A supercooled metal sleeve can be slipped around two pipe ends and bond them together by contracting as it warms to room temperature. Such a method replaces welding, screws and other fasteners.

"This is an entirely open-ended technology," said Thomas W. Duerig, manager of metals research at the Raychem Corporation, a large high-technology materials company in Menlo Park, Calif., and a leader in the field. "I don't see an end to its uses."

Shape-memory metals were discovered about 50 years ago, advanced by the Navy in the 1960's and used in some aerospace applications during the 1970's. But only in the last two years has the wide commercial potential been recognized outside of research labs. Major efforts to capitalize on the technology are under way in Japan, China, Belgium, Britain and the United States.



John Segal

Westinghouse has chosen the technology for some electrical equipment. I.B.M. is studying it for electrical fasteners. Sharp and others are developing it for consumer products in Japan. One new company, Memory Metals Inc. of Stamford, Conn., bases its entire business on the technology. Raychem says its sales are about $10 million a year, the industry's largest. Others put potential industry sales at hundreds of millions of dollars a year.

"The market is in its infancy," said C. Marvin Wayman, a professor of metallurgy at the University of Illinois/Urbana-Champaign and an expert in the technology.

• • •

The most common alloys are titanium-nickel and copper-zinc-aluminum (aluminum brass). At certain temperatures, the crystal lattice structure of the material changes dramatically, causing a change in shape. Some expand, contract, bend or unbend. The change is lightning quick: thousands of feet per second, said L. McDonald Schetky, Memory Metals' president and former materials research head at M.I.T.'s instrument laboratory. Depending on the materials and their size, the temperature at which a shape changes varies from 275 degrees below zero to 500 degrees above zero.

One new use for these metals is in operating windows of greenhouses and farm buildings. Memory Metals has devised a water shutoff to prevent shower scalding. The metals can also activate building sprinkler systems for fires faster than conventional methods.

The metals are also used in circuit breakers that reset themselves when the wires cool. In robot hands, the metals move fingers by expanding and contracting as electric current is switched on and off. They replace motors and gears, thus sharply reducing robot weight. In the Grumman F-14 fighter jet, a memory metal attaches hydraulic lines where heat or vibration would make welding or screws risky. Raychem uses the technology in air conditioners and nuclear power plants.

The metals can be made so that they will not revert and break a bond under all foreseeable operations. The cost is often similar to existing methods and sometimes cheaper.

Medical uses include a small tube — inserted into the body by a catheter — that expands when it reaches body temperature, reinforcing an artery's wall. Brassiere companies are studying the metals to replace steel as supports and continually restore the bra to its original shape when worn. Engines are being designed to use memory metals and run on heat, from power plant effluent or from the sun in third world villages, instead of electricity. The metals would be exposed to heat on one side and cool water on the other, causing continual motion.

Dr. Frederick E. Wang, president of Innovative Technology Inc., of Beltsville, Md., used a memory metal to make a toy boat that sold for $22 as a Christmas present. Dr. Wang, a physicist, has devised practical engines, too. Of the technology, he said, people "see it, but they don't believe it."