Discussion 22

GORTER: Using the gamma and the critical temperature of this last alloy and assuming a parabolic law, can you calculate the critical field?

R. A. HEIN, *Naval Research Laboratory:* We tried to measure the critical fields. We can't put a magnetic field on because we're in a mu-metal case. What we do, however, is to observe the susceptibility as a function of the measuring field, and in that way we can tell what measuring field will cause it to go normal. We can then estimate the critical field at absolute zero to be about 2.7 G.

J. W. GARLAND, *Institute for the Study of Metals:* I would just like to point out that perhaps one does not really expect V to be a constant, since V is a screened interaction and the density of states is changing by such a large amount. The interaction that one would expect to be more nearly a constant is the unscreened interaction. When one attempts to calculate this, one finds this is even more nearly constant varying by only 10% or 15% from one side of the transition-metal group to the other, except at the very end where it drops rapidly. This is just an empirical calculation based upon the experimental data only, and not a theoretical calculation.

Brillouin Zone Effects in Superconductivity*

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INTRODUCTION

When the Fermi surface of a metal approaches, touches, or overlaps the boundary of a Brillouin zone, some sort of electron–lattice interaction[1] may be expected. The small discontinuities in physical properties which result from the interaction are known as "Brillouin zone effects." Such an effect, for example, has been observed by Levinson[2] in a study of the lattice parameter of Li–Mg alloys. The Brillouin zone effects described here were discovered accidentally in the course of investigating the composition dependence of superconducting transition temperature (T_c) in binary alloy systems. Although the effect of Brillouin zone interactions on transition temperature had not been observed prior to this work, they give rise to anomalies which are easily seen on T_c vs composition plots. Since T_c is easy to measure, superconductivity provides a rapid and convenient way to discover the effects and determine accurately the critical compositions. Knowledge of these compositions gives information on the geometry of Fermi surfaces in alloys—information which is otherwise rather difficult to obtain. The Brillouin zone effects are also of interest for their own sake in metal physics.

Also of interest, but still some time in the future, is the use of the observed variation of T_c at the Brillouin zone effect compositions, where the Fermi surface geometry and connectivity are changing from one (hopefully) known state to another known state, to obtain information about the interactions responsible for the superconductivity.

We have found Brillouin zone effects so far in an intermediate phase of the Hg–In alloy system[3,4] and in the indium-rich terminal solid solutions of the In–Sn and In–Pb systems.[5,6] In the Hg–In case (Fig. 1) nothing can be said about the electronic details, since the crystal structure of the phase has not yet been solved, and consequently not even the Brillouin zone geometry is known. X-ray diffraction patterns have been obtained on alloys straddling the composition where the superconductivity anomaly appears, and these patterns, together with thermal-analysis data, verify that the superconductivity anomaly does not correspond to a phase change.[3] Because of experimental difficulties it has not been possible to make a detailed study of lattice parameter vs composition through the anomaly. This is unfortunate, since the superconductivity anomaly is quite large. A discontinuity in T_c itself as well as dT_c/dx, is easily resolved, and in fact [Fig. 1(b)] two transitions are observed over a range of composition, indicating the presence of two electronic phases.

In the In–Sn and In–Pb cases (Fig. 2) somewhat

* Research supported in part by the U. S. Air Force Office of Scientific Research and the National Science Foundation.

[1] If the interaction is too strong, a phase change will, of course, result as in the noble metal alloy systems which obey the Hume–Rothery rules.

[2] D. W. Levinson, Acta Met. **3**, 294 (1955).

[3] B. R. Coles, M. F. Merriam, and Z. Fisk, J. Less-Common Metals **5**, 41 (1963).

[4] M. F. Merriam, M. A. Jensen, and B. R. Coles, Phys. Rev. **130**, 1719 (1963).

[5] M. F. Merriam and M. von Herzen, Phys. Rev. **131**, 637 (1963).

[6] M. F. Merriam, Phys. Rev. Letters **11**, 321 (1963).

more can be said about the electronic details since not only is the crystallography well known[7] but also the Fermi surface geometry of pure indium has been investigated by the magnetoacoustic method.[8] These systems (In–Sn and In–Pb) moreover are well suited to high precision lattice parameter determinations. It was therefore possible, having first pinpointed the

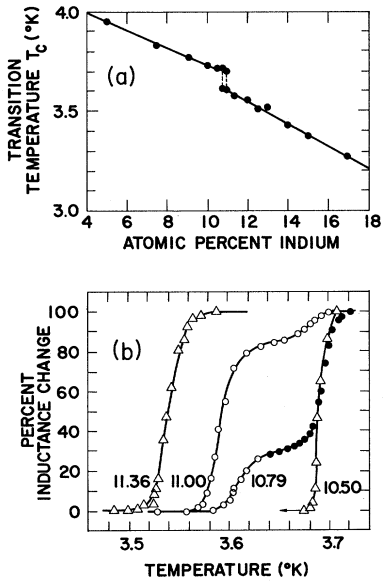

FIG. 1. (a) Transition temperature as a function of composition in the β phase of the Hg–In system, showing discontinuity in both T_c and dT_c/dx (x = at. % In). The vertical dotted lines connect two transitions occurring in a single sample. (b) Superconducting transitions of alloys in the neighborhood of the critical composition. Two transitions are resolved in the samples with 10.79 and 11.00 at. % indium, demonstrating the existence of two electronic phases.

appropriate compositions with the transition temperature measurements, to study carefully the effect of the Fermi surface–Brillouin zone interaction on the equilibrium atomic separation (Fig. 3).

EXPERIMENTAL

Careful annealing of all samples prior to the superconductivity measurements was found to be essential, in order to avoid the quench effect.[5] The In–Sn and In–Pb samples, for example, were annealed at 120°C for at least a week. Transition temperatures were determined with ac inductance methods[4,5] in essentially zero magnetic field. The lattice parameter data shown in Fig. 3 were obtained at room temperature on filings taken from the ingots which had previously served as samples for the superconductivity tests. The filings were annealed at 120°C for 2 days in a He atmosphere just prior to measurement, in order to be sure of retaining the In phase. An internal standard (SiC) was used.

The diffractometer[9] was operated in a step scanning mode in steps of 0.01 deg 2θ. This procedure, which successfully resolved the $K\alpha$ doublet in the reflections (202 and 103) used to determine the lattice parameters, was necessary because of the grain size in the annealed filings. Earlier lattice parameter measurements on In–Sn[10] and In–Pb[11] alloys did not detect the anomaly shown in Fig. 3.

DISCUSSION

In the past, Brillouin zone effects in solid solutions have been studied mainly through lattice parameter measurements. A number of calculations of lattice parameter variations have been made[12]; we consider the analysis of Goodenough.[13] If the Fermi surface is quite close to, but not touching, a zone boundary then the average energy of the conduction electrons can be lowered by a contraction of the zone, corresponding to an expansion of the space lattice. After the Fermi surface actually contacts the zone face a force in the opposite direction is set up, which, as the Fermi surface continues to expand, results in a contraction of the space lattice. This contraction continues until the onset of overlap, which tends again to expand the lattice, the expansion progressively saturating with increasing overlap.

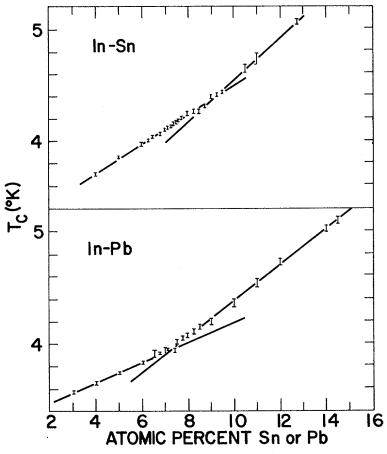

FIG. 2. Superconducting transition temperature vs composition for solutions of Pb and Sn in In. The spreads shown are total transition widths and do not indicate experimental error.

The several stages of the interaction described by Goodenough are apparently reflected in the lattice

[7] W. B. Pearson, in *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), pp. 696–699.
[8] J. A. Rayne, Phys. Rev. **129**, 652 (1963).
[9] GE XRD-5, copper radiation, made available through the generosity of G. O. S. Arrhenius.
[10] C. G. Fink, E. R. Jette, S. Katz, and F. J. Schnettler, Trans. Electrochem. Soc. **88**, 229 (1945).
[11] A. Moore, J. Graham, G. K. Williamson, and G. V. Raynor, Acta. Met. **3**, 579 (1955).
[12] T. B. Massalski and H. W. King, in *Progress in Materials Science* (Pergamon Press, Inc., New York, 1961), Vol. 10, p. 62.
[13] J. B. Goodenough, Phys. Rev. **89**, 282 (1953).

parameters of the In–Sn alloys (Fig. 3). The variation of the parameters of the In–Pb alloys is more complicated at least in the case of the a parameter. There is a possibility that the In–Sn a parameter would take the form of the In–Pb parameter if data points were available between 7 and 7.5 at. % Sn.

We now consider the question of which Brillouin zone faces are involved.[14] The form of the actual Fermi surface of pure In is highly relevant. Rayne[8] has interpreted his magnetoacoustic measurements on In as confirming the main features of a Fermi surface calculated on the free electron model, i.e., a full first zone, a second zone partially filled with electrons, and small arms of electrons extending into the third zone. It seems possible, however, to interpret his smaller extremal dimensions as arising from first zone holes, rather than third zone electrons. In this case there might be no electrons at all in the third zone for pure In. Rayne's failure to observe any neck orbits associated with the second zone, which should be present if there are electrons in the third zone, is then readily understood. If the Fermi surface of In is, in fact, contained within the first two zones, then the lattice parameter anomalies are easily interpreted as arising from the interaction of an expanding Fermi surface with the boundary of the second zone (in the neighborhood of the first zone–second zone–third zone common points) and subsequent overlap into the third zone. First-zone holes would be wiped out early in the process. It is interesting to note that Tomasch and Reitz[15] have independently interpreted their thermopower measurements on In–Pb alloys by invoking first extinction of holes, then contact with a zone face followed by overlap at about 7 at. % Pb.

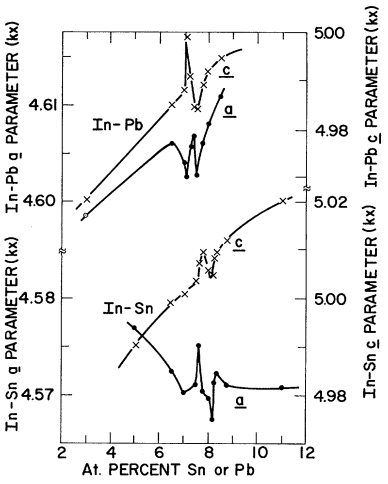

FIG. 3. Lattice parameters as a function of composition in indium primary solid solutions containing Sn and Pb. Note that the a parameters are plotted to twice the scale of the c parameters.

Returning now to the superconductivity anomalies we note that the discontinuities in T_c and dT_c/dx in both Hg–In (Fig. 1) and In–Sn, In–Pb (Fig. 2) are small compared to those which typically result from crystallographic phase changes in these alloy systems.[4,5] This would be expected if the T_c values are reflecting a density of states variation, since the density of states change accompanying an electronic phase change would be expected to be much smaller than that accompanying a crystallographic phase change. We have not as yet measured the density of states of any of our samples in any independent way.

It is interesting to note that the contact with the zone face takes place at a measurably lower tetravalent atom concentration in In–Pb alloys than in In–Sn. Furthermore, in spite of a careful search, no effect was found in In–Bi alloys up to 7% Bi, whereas one would have been expected at about 4%, since Bi is pentavalent. Presumably, a Bi atom dissolved in In ionizes incompletely.

All but one of the other alloy systems having known lattice parameter anomalies[16] specifically identifiable with Brillouin zone interactions are not superconducting above 1°K. One known lattice parameter anomaly[17] in a superconducting Sn-rich solid solution is apparently not accompanied by a detectable change in superconducting transition temperature.[18] This lattice parameter anomaly is, however, not thought to result from an expanding Fermi surface meeting a zone boundary in the usual way, but reflects a somewhat different situation.[16]

The major results and conclusions of this work then are (1) The influence of a Fermi surface Brillouin zone interaction is seen, for the first time, in the superconducting transition temperature. (2) The characteristic variation of lattice parameters caused by an expanding Fermi surface interacting with a Brillouin zone is observed for the first time in a polyvalent nontransition metal. (3) The structure observed by Tomasch and Reitz in thermopower measurements on In–Pb alloys is confirmed by measurements of other properties and their quali-

[14] A helpful illustration, showing the first and second zones for an fcc lattice (In is distorted fcc), can be found in F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 299.

[15] W. J. Tomasch and J. R. Reitz, Phys. Rev. 111, 757 (1958).

[16] W. B. Pearson, in *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), pp. 38–54.

[17] J. A. Lee and G. V. Raynor, Proc. Phys. Soc. (London) B67, 737 (1954).

[18] B. R. Coles, IBM J. Res. Develop. 6, 68 (1962); B. R. Coles and S. Wipf (unpublished).

tative interpretations supported. (4) The Fermi surface of In may not resemble the free electron model as closely as had been previously thought, possibly having holes in the first zone and no electrons in the third zone.

Discussion 23

COLES: Mr. D. Farrell at Imperial College has found strong correlations between transition temperature and the occurrence of a Fermi-surface overlap in cp hexagonal phases based on zinc and cadmium.

ACKNOWLEDGMENTS

The encouragement and counsel of B. T. Matthias, B. R. Coles and G. O. S. Arrhenius is gratefully acknowledged. Sharon Hillhouse provided valuable experimental assistance.

Superconductivity in the Y–Rh and Y–Ir Systems

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We are trying to decide whether a critical condition for the occurrence of superconductivity exists or whether all nonferromagnetic metals will eventually become superconducting. By *eventually* we mean of sufficiently high purity and sufficiently low temperature. During the past five years it has become very likely that superconductivity seems to be the rule rather than the exception, and any critical condition may be purely theoretical. From symmetry considerations the transition temperatures of Sc, Y, and Rh will be rather low. As shown by Hamilton and Jensen[1] the superconducting temperatures of the transition elements are entirely symmetric with respect to the 6th column of the periodic system. Thus, Y will correspond to Rh and Sc to Co, if the latter were not ferromagnetic. La is a high-temperature superconductor *only* due to the vicinity of 4*f* levels and would otherwise correspond to Ir, a superconductor at 0.14°K. Since the 3rd and 9th columns are thus bracketing the range of high transition temperatures, one would now expect that most combinations of the 3rd with the 9th column would result in phases with transition temperatures higher than the elements in these columns. We have shown this to be so, thus strengthening our hypothesis as to the generality of superconductivity. The occurrence of superconductivity in the Y–Rh and the Y–Ir system is shown in Figs. 1 and 2. While the two systems are not isomorphous, between the two of them virtually the

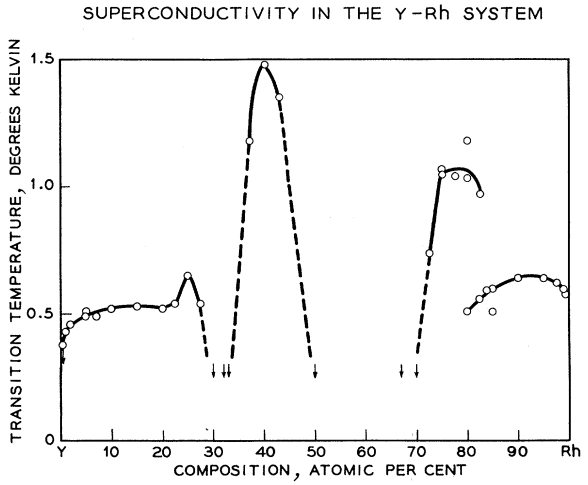

FIG. 1. Superconductivity in the Y–Rh system.

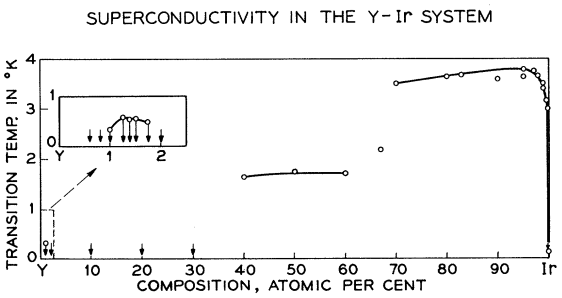

FIG. 2. Superconductivity in the Y–Ir system.

[1] D. C. Hamilton and M. Anthony Jensen, Phys. Rev. Letters, 11, 205 (1963).