PHYSICAL REVIEW VOLUME 104, NUMBER 6 DECEMBER 15, 1956

Letters to the Editor

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Evidence for Vacancy Mechanism in Intermetallic Diffusion*

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(Received October 29, 1956)

It has been suggested[1] that in a binary ordered alloy of the type AB, in which every atom is surrounded by unlike atoms, it should be possible to decide experimentally between the interstitial and vacancy mechanisms of self-diffusion. For if atoms move by nearest-neighbor jumps, then a vacancy mechanism leads to equal diffusion coefficients for both species, whereas there would be no such equality for the migration of atoms interstitially. Earlier results on diffusion in the ordered alloy NiAl by Berkowitz, Jaumot, and Nix[2] could not be utilized to test this idea because the diffusion of only one tracer was measured and because the Al atom cannot reside on a Ni site, thereby raising doubt in this case as to whether both atoms move by nearest-neighbor jumps. Recent data by Kuper, Lazarus, Manning, and Tomizuka[3] on self-diffusion in CuZn, however, may be analyzed from this point of view. The results appear to provide strong evidence for the vacancy mechanism.

Denote the ratio of the coefficients of self-diffusion, $D(\mathrm{Zn})/D(\mathrm{Cu})$, by G. Consider the alloy to be stoichiometric (atomic concentration $=0.5$). The prediction that G be unity for a vacancy mechanism applies only to the case of the perfectly ordered alloy, whereas at even the lowest temperature at which Kuper *et al.* could study diffusion the long-range order parameter s is still only about 0.9. We have made an approximate estimate of the behavior of G when s is less than 1 in the following manner. Let J be the ratio of the jump probability of a particular Zn atom into an already existing adjacent vacancy to the jump probability for a Cu atom, and let $p(\mathrm{Cu}, \alpha)$ be the probability that a given α site is occupied by a Cu atom. Then the probability that a β vacancy becomes occupied by a Cu atom is proportional to $p(\mathrm{Cu}, \alpha)$, and the probability that it becomes occupied by a Zn atom is proportional to $J\cdot p(\mathrm{Zn}, \alpha)$. Expressing the p's in terms of s [$p(\mathrm{Cu}, \alpha)=\frac{1}{2}(1+s)$, etc.] and remembering that a vacancy will be on an α site half the time and on a β site half the time, we find that

$$G=\frac{(\text{total number of jumps per Zn atom})}{(\text{total number of jumps per Cu atom})}=\frac{J(1+J+s^2-Js^2)}{(1+J-s^2+Js^2)}.$$

Now J is expected to depend on s and the temperature T. We estimate J by taking the ratio of the temperature-dependent diffusion coefficients in the high-temperature, disordered phase:

$$J=[D_0(\mathrm{Zn})/D_0(\mathrm{Cu})]\exp[(H_{\mathrm{Cu}}-H_{\mathrm{Zn}})/RT].$$

This should be a satisfactory approximation if s is not large; at large s the value of G approaches 1 for any value of J.

Using the high-temperature results of Kuper *et al.* to estimate $J(T)$ and the data of Chipman and Warren[4] to obtain $s(T)$, the predicted dependence of G upon s for beta brass is plotted as the solid line in Fig. 1. The experimental results of Kuper *et al.* below the ordering temperature are shown as circles. Considering that there are no adjustable parameters in the theoretical expression, that no corrections have been made for the fact that the alloy of Kuper *et al.* was actually about 47 atomic % Zn, and that the differences between experimental and predicted results lie within experimental errors in s and G, the agreement appears satisfactory. A formalistic modification of our expression for G for the case of nonstoichiometric composition produced only a negligible change from our simpler treatment. The effect of s on J was neglected. This could very well be justified for a 50:50 alloy, but may not be sound for a nonstoichiometric case. Within the present order of approximation it was also assumed that the effect of correlated jumps is negligible even when the value of s lies in the intermediate range where this effect may be significant.

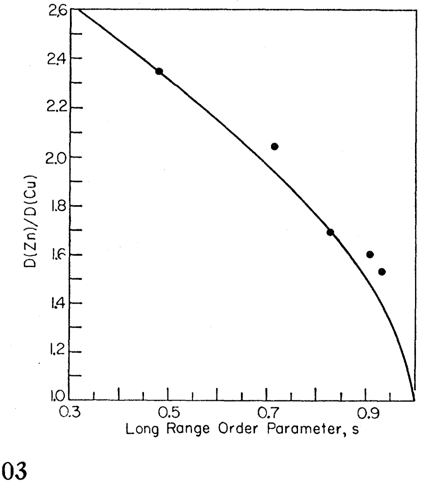

FIG. 1. The calculated dependence of G on s for beta brass (solid line). Experimental results are shown as dots.

It appears that the results of the diffusion of antimony in CuZn, which can be explained in terms of the interstitialcy mechanism, require further experimental confirmation. At present, there are only three points in the ordered phase. It is also necessary to investigate the diffusion of other impurities before definite conclusions can be drawn as to the behavior of the impurity atoms in the ordered lattice.

It is therefore proposed that these experiments on beta brass constitute convincing evidence for the vacancy mechanism.

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* Supported in part by the U. S. Atomic Energy Commission and by the U. S. Air Force.

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Infrared Cyclotron Resonance in Bi, InSb, and InAs with High Pulsed Magnetic Fields*

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(Received October 29, 1956)

MICROWAVE cyclotron resonance in materials[1] other than germanium and silicon is not well defined because of large scattering or plasma effects. The use of infrared frequencies solves both problems, since $\omega\tau \gg 1$ even at room temperatures, and $\omega > \omega_p$ for semiconductors and semimetals. ω and ω_p are the frequencies of the electromagnetic field and the plasma, respectively, and τ is the scattering time. Infrared experiments, however, require high magnetic fields. The first successful results were obtained for InSb by Burstein, Picus, and Gebbie[2] with a Bitter magnet up to 60 000 gauss at 41.1 μ. Our experiments on InSb and InAs were performed from 10 to 22 μ with pulsed fields up to 320 000 gauss at room temperature, using both transmission and reflection techniques. The first direct observation of cyclotron resonance in a metal, Bi, was also made.

The samples were mounted in special coils[3] located between the infrared source and the monochromator. The detector,[4] a zinc-doped germanium cube maintained at 4.2°K, was located six feet from the coil to reduce electromagnetic pickup. The output signal from the high-impedance detector was fed to a cathode follower circuit specially designed to reduce the effective lead capacitance to give a time constant of 2 μsec. The output was recorded by photographing an oscilloscope trace, triggered by light from the spark gap switch of the pulse magnet.[3]

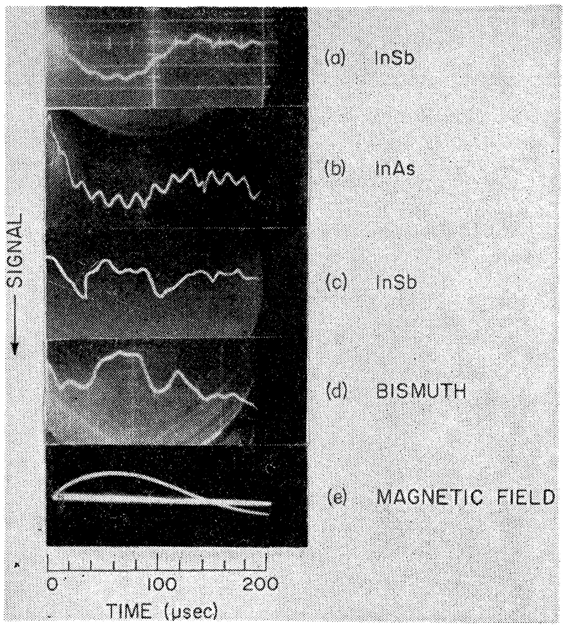

FIG. 1. Cyclotron resonance traces. Transmission signal through 200 μ samples at $\lambda = 12.7\ \mu$: (a) InSb, $B_{\max} = 220$ kilogauss; (b) InAs, $B_{\max} = 295$ kilogauss. Reflection signal at $\lambda = 18.3\ \mu$ and $B_{\max} = 155$ kilogauss: (c) InSb, (d) bismuth. Magnetic field trace *vs* time is shown by curve (e).

The photograph in Fig. 1 shows traces of relative transmission of 200 μ thick InSb and InAs samples at 12.7 μ during a field pulse. The peak field for resonance was higher in InAs; the trace is modulated by periodic high-frequency noise. Even with fields up to 300 000 gauss, the resonance is not resolved in InSb, where the mass is presumably small. Two possible factors contributing to the excessive width of the resonance absorption are: (1) dimensional broadening due to the sample thickness exceeding the skin depth (10 μ) at resonance, (2) the apparent increase of the effective mass with increasing magnetic field. The first effect can be eliminated by using reflection techniques. A typical reflection trace for InSb is shown in Fig. 1(c). We interpret the resonance field as that corresponding to the point at which the rapid change of reflection passes through zero. By determining the resonance magnetic field from a calibrated trace shown in Fig. 1(e) for different wavelengths, a plot of effective mass *versus* magnetic field is obtained. This relation is shown for InSb in Fig. 2. Masses determined by Burstein *et al.*[2] and microwave cyclotron resonance at lower fields are also included. The increase of m^* for InSb is presumably related to decreasing curvature of the band with increasing energy, and correlates well with the data of Chasmar and Stratton[5] from thermoelectric power measurements. Reflection experiments were also performed recently on InAs, yielding $m^* \approx 0.03m_0$ between 150 000 gauss and 250 000 gauss. Further experiments