

($x_0 = x_i$), the average moment would be 1.66 Bohr magnetons per atom of iron. On the other hand, if it is assumed, as was predicted² by Néel and by Verwey (on the basis of x-ray studies) that there is a selective iron vacancy formation limited to octahedral sites ($x_i = 1$) the average moment is 1.25 Bohr magnetons per atom of iron for pure Fe_2O_3 . For a sample of the described composition, the average moment would be 1.19 Bohr magnetons per atom of iron. Our results of 1.18 ± 0.02 Bohr magnetons per atom of iron is in good agreement with this theoretical value for a restricted distribution. That is, in view of the 1.66 Bohr magnetons per atom required for a random distribution

and 1.19 required for deficiencies restricted to octahedral sites, it can be said that the magnetization experiment supports the preferential distribution. An alternative possibility, based on hydrogen atoms in the lattice on octahedral sites, has been suggested by Braun.⁶ The resulting moment (one Bohr magneton per atom of iron) would, however, not be in keeping with the moment obtained in the present investigation. Further study is being made of magnetic properties of oxygenated compounds of iron. Our appreciation is extended to Mr. Dean Walter of the Naval Research Laboratory for analysis of the samples.

⁶ P. B. Braun, *Nature* **170**, 1123 (1952).

Significance of Hall Effect Measurements on Alloys*

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Hall effect data for a number of alloys are examined in the light of the accepted theory of this effect. It is concluded that assumptions made about the relaxation time which seem appropriate when scattering by lattice vibrations predominates are not valid when scattering by solute atoms becomes significant.

IN recent years a number of investigations of the variation of the Hall constant (R) as a function of composition in alloys have been carried out. In particular, a series of papers by Pugh and his co-workers¹⁻³ has shown that important indications of the electronic structures of ferromagnetic transition metal alloys can be obtained from such measurements.

It is well known that the Hall constant is related to n , the number of electrons per atom, by the expression

$$R = 1/(Nnec),$$

where e is the electronic charge, c the velocity of light, and N the number of atoms per unit volume, only for metals in which the Fermi surface takes certain simple forms. Even in the noble metals, which have one conduction electron per atom and a half-full Brillouin zone, the value of n^* [defined as $1/(RNec)$] is not exactly 1.0. Recent measurements of the thermoelectric powers of silver alloys⁴ in which the number of conduction electrons has been reduced to slightly less than 1.0 per atom suggest strongly that the anomalously positive sign of the thermoelectric power of pure silver is due to the presence of electrons in states near some Brillouin zone boundary where the energy departs from the free-

electron value. The occupation of such states by the electrons of highest energy is probably also responsible for the departure of n^* from unity. The present note is intended to draw attention to evidence that in alloys R departs from the free-electron value to an extent that cannot reasonably be explained in terms of distortions of the Fermi surface. There are strong grounds for believing that when both lattice scattering and impurity scattering are present, discussions of Hall effect data must take the scattering mechanisms into account.

Hall effect data are available for the silver-gold alloys over a wide range of compositions and temperatures,⁵ and n^* values derived from them are shown in Fig. 1. The room temperature values for the alloys are greater than those of the pure metals, but it is conceivable that these increases are due to increases in the Fermi surface distortions present in the pure metals. At low temperatures, however, n^* becomes still greater for the alloys, while approaching unity for the pure metals. This peculiar temperature variation and the very large low-temperature values show clearly that in the alloys there exists some factor, not present in the pure metals, which plays an important part in determining the value of R .

By adding 40 atomic percent of palladium to silver, the number of conduction electrons can be reduced to 0.6 per atom without d -band holes being created. These electrons might be expected to be described extremely

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¹ A. I. Schindler and E. M. Pugh, *Phys. Rev.* **89**, 295 (1953).

² S. Foner and E. M. Pugh, *Phys. Rev.* **91**, 20 (1953).

³ E. M. Pugh, *Phys. Rev.* **97**, 647 (1955).

⁴ J. C. Taylor and B. R. Coles, *Phys. Rev.* **99**, 614 (1955). (Further details of this work will be published shortly.)

⁵ K. Onnes and B. Beckman, *Proc. Acad. Sci. Amsterdam* **15**, 307, 319, 664 (1912).

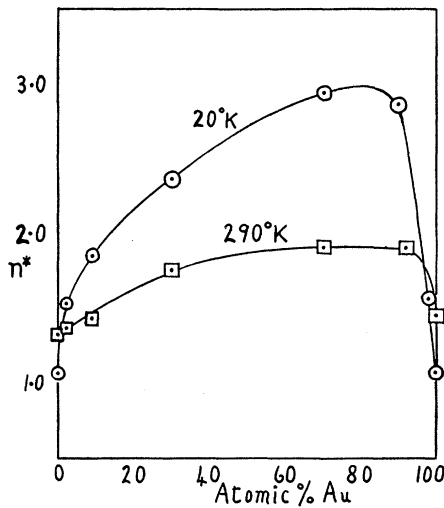


FIG. 1. n^* values for silver-gold alloys at room and liquid hydrogen temperatures.

well by a free-electron model, since the states of highest energy are remote from zone boundaries, and the thermoelectric properties⁴ seem to bear out this expectation. The Hall constant of this alloy is therefore of great interest, for were distortions of the Fermi surface the only factor making n^* different from n , these two quantities should be accurately the same in this alloy. The value of n is certainly 0.6, but the measurements of Wortman⁶ and Schindler⁷ give n^* values of 0.4 or less at room temperature.

If n^* were dependent only on the electronic structure and not on the nature of the scattering processes, it should change smoothly with composition in the alloy series cobalt-nickel, nickel-copper; provided, of course, that a collective band treatment is appropriate for all the electrons involved in transport effects. The experimentally derived values⁸ show, however, a marked cusp at pure nickel. In any such alloy series of a metal with its neighboring elements in the periodic table, n^* should change smoothly with composition, but those results which are available do not show such behavior. Figure 2 shows those derived from measurements on dilute alloys of silver with palladium, cadmium, tin, and antimony⁹;

⁶ J. Wortman, *Ann. Physik* **18**, 233 (1933).

⁷ A. I. Schindler, *Phys. Rev.* **94**, 1422 (1954). (The author's thanks are due to Dr. Schindler for details of his results prior to publication.)

⁸ Y. G. Dorfman and P. N. Zhukova, *Zhur. Eksptl. i Teort. Fiz.* **9**, 51 (1939).

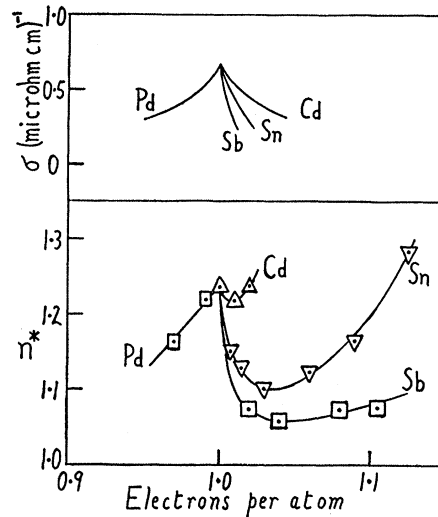


FIG. 2. Values of conductivity (σ) and n^* at room temperature for dilute alloys of Pd, Cd, Sn, and Sb in silver. The results are plotted against the mean number of conduction electrons per atom.

these elements have atomic numbers of -1 , $+1$, $+3$, and $+4$ relative to silver, and the results are plotted against the mean number of conduction electrons per atom. These results are strong evidence in favor of the suggestion that the Hall effect depends on the scattering mechanism, for this is purely thermal in pure silver while only partly so in the alloys. Electrical conductivity data⁹ are shown for comparison.

In the light of the above evidence, it is suggested that some assumption, other than that of a simple Fermi surface, made when deriving R - n relationships is at fault in alloys. It is likely that this is the assumption that the time of relaxation is a function of energy only, since this parameter has a different character in alloys from that which it possesses in pure metals. The different effects produced in silver by gold (a homovalent impurity) and by the heterovalent impurities suggest that theoretical treatments would have to consider the scattering mechanisms in some detail.

The dependence of measured Hall effects on the relative proportions of lattice and impurity scattering is being further investigated in various alloy systems.

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⁹ J. O. Linde, *Ann. Physik* **14**, 353 (1932).