

Fe⁵⁷ Mössbauer Effect in Cu-Ni Alloys

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The Mössbauer effect of Fe⁵⁷ has been used to study the properties of iron impurity atoms in the complete range of composition of Cu-Ni alloys. The isomer shift indicates a small decrease in the total electronic density at the Fe⁵⁷ nucleus in going from pure Ni to pure Cu. The magnetic field at the iron nucleus at 0°K decreases by 9% in the range from 0 to 40% Cu. Both results show that only minor changes take place in the atomic configuration of the iron. The linewidth, measured in the paramagnetic alloys, is smallest in pure copper and largest near the middle of the composition range. The rapid change in linewidth with small nickel admixture can result from quadrupole splitting due to the field gradients arising from the spatial charge fluctuations around an impurity atom. Some of the broadening can also arise from an inhomogeneous isomer shift due to a range of surroundings of an iron atom in the alloy.

INTRODUCTION

A STUDY of the Mössbauer effect¹ of Fe⁵⁷ atoms dilutely dispersed in metallic cobalt and nickel² has shown that the magnetic field at the iron nucleus is little changed by these environments relative to its value in metallic iron.³ Values in the vicinity of -3×10^5 oe have been obtained in these ferromagnetic elements. The sign of the field has actually been obtained only in the case of iron⁴ but it may be assumed to be the same in all three cases. It suggests that the major contribution to the field arises from the exchange polarization of the 3s by the 3d electrons. Measurements of the isomer shift⁵ show that there is also little difference in the total electronic density at the nucleus of an iron atom in the transition metals.⁶

The ability of Cu to fill the *d* band in Cu-Ni alloys⁷ suggests that the behavior of dilutely dispersed iron in these alloys may contribute to our understanding of the apparent stability of the iron *d*-shell configuration. It is known from both susceptibility⁸ and nuclear magnetic resonance⁹ (NMR) measurements that iron dispersed in Cu behaves like a paramagnetic ion, but details of the behavior are not understood. These include (1) the dependence of the moment per Fe atom on concentration in the susceptibility measurements⁸ and (2) an anomalous behavior below 20°K in the NMR measurements.⁹ It is possible that these effects arise from the low solubility of Fe in pure Cu which necessitated the use of quenched, supersaturated alloys in both of these measurements. The Mössbauer effect, on the other hand,

makes it possible to study the behavior of very dilute solid solutions of Fe in Cu. Moreover, the solubility of Fe is greatly increased by the presence of Ni.

EXPERIMENTAL

The specimens were prepared by melting together 99.999% pure Cu and 99.99% pure Ni in a quartz crucible under an argon atmosphere. Slices were cut from the resulting ingots with a rubber-bonded abrasive wheel (to minimize iron contamination) and polished. A small amount of Co⁵⁷Cl₂ solution was evaporated to dryness on a polished face, and the slice heated to 900°C for 45 min in an atmosphere of hydrogen. The surface was then repolished to remove surface contamination. The experiments were carried out in equipment described elsewhere.¹⁰ The iron atoms under study are produced by the electron-capture decay of the Co⁵⁷.

ISOMER SHIFT

The isomer shift, i.e., the displacement of the centroid of the gamma-ray absorption from zero Doppler velocity, was measured with respect to a potassium ferrocyanide absorber made of isotopically enriched Fe⁵⁷. The absorber was kept at room temperature. The positive sign of the measured shift (0.026 cm/sec for pure Cu at 300°K) indicates that the nuclear transition energy in the alloy is greater than that in the absorber. In a previous publication,⁶ room-temperature isomer shifts measured with respect to type-310 stainless steel were reported for a wide range of materials. The isomer shift of potassium ferrocyanide with respect to stainless steel was given as 0.008 cm/sec, allowing a direct comparison with the earlier 300°K results. The shift for Fe⁵⁷ in Cu at room temperature with respect to stainless steel is then 0.034 cm/sec. This value may be compared with a value of 0.015 cm/sec characteristic of Fe⁵⁷ in iron or nickel. Referring to Fig. 1 of reference 6, it is apparent that this shift corresponds to a *small* change in the total electronic density at the nucleus, and therefore in the atomic configuration of the iron. It is considered unlikely that major changes occur which almost

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⁴ S. S. Hanna, J. Heberle, G. J. Perlow, R. S. Preston, and D. H. Vincent, *Phys. Rev. Letters* **4**, 513 (1960).

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⁷ R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951).

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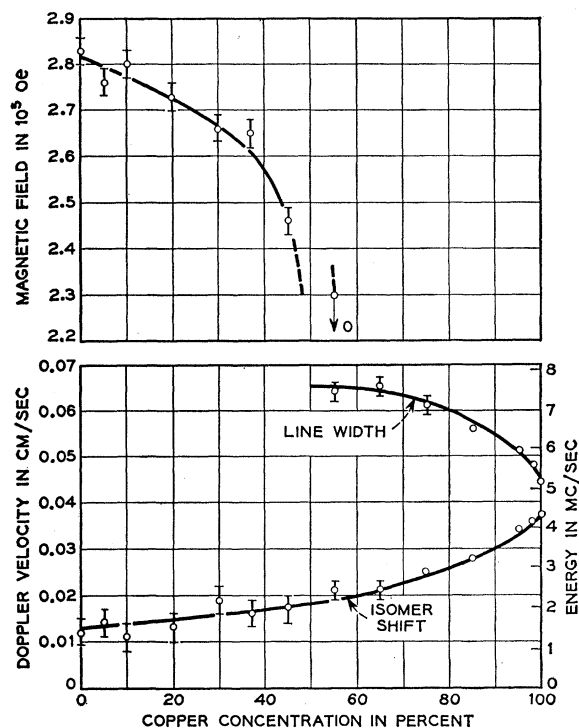


FIG. 1. Magnetic field at the iron nucleus, isomer shift, and Mössbauer effect linewidth at 0°K for Fe^{57} atoms dilutely dispersed in Cu-Ni alloys, plotted as a function of alloy composition (in atom percent of copper).

exactly compensate insofar as their effects on both the charge density at the nucleus and the magnetic field at the nucleus (see below) are concerned.

Figure 1 gives the 4°K shifts for the complete range of composition from pure nickel to pure copper measured with respect to potassium ferrocyanide. The results correspond to a decrease in the electronic density at the nucleus with increasing copper concentration, which could arise from increased shielding of the 3s electrons by the 3d electrons. It is of interest to note that the rate of change of the isomer shift correlates with the rate of motion of the Fermi level in the alloys, when both are considered as functions of composition.

It is by no means clear, however, that the entire effect on the isomer shift arises through the mechanism suggested. There is a small increase in lattice parameter in going from nickel (3.517 Å) to copper (3.608 Å) which could also produce significant changes in the electronic wave functions.

FIELD AT THE NUCLEUS

The hyperfine structure of the Fe^{57} in the ferromagnetic Cu-Ni alloys was determined at 4°K and the field at the nucleus deduced from the ground-state splitting which is independent of possible quadrupolar effects (see below). The equipment was calibrated in terms of the corresponding splitting in metallic iron. The data,

TABLE I. Field at the nucleus, isomer shift, and linewidth at 0°K for Fe^{57} atoms dilutely dispersed in Cu-Ni alloys.

Alloy composition (At. % Cu)	H at 0°K Fe nucleus (10^5 oe)	Isomer shift (cm/sec)	Linewidth (cm/sec)
Pure Ni	2.83 ± 0.003	0.012 ± 0.003	...
5.0	2.76 ± 0.003	0.014 ± 0.003	...
10.0	2.80 ± 0.003	0.011 ± 0.003	...
20.0	2.73 ± 0.003	0.013 ± 0.003	...
30.0	2.66 ± 0.003	0.019 ± 0.003	...
37.0	2.65 ± 0.003	0.016 ± 0.003	...
45.0	2.46 ± 0.004	0.017 ± 0.003	...
55.0	~ 0	0.021 ± 0.002	0.064 ± 0.002
65.0	...	0.021 ± 0.002	0.065 ± 0.002
75.0	...	0.025 ± 0.001	0.061 ± 0.002
85.0	...	0.028 ± 0.001	0.056 ± 0.001
95.0	...	0.034 ± 0.001	0.051 ± 0.001
98.0	...	0.036 ± 0.001	0.048 ± 0.001
99.999	...	0.037 ± 0.001	0.044 ± 0.001

Table I, show that the field is only weakly dependent on composition from 0 to 40% Cu. Beyond this point the field decreases rapidly and has become zero at 55%. The Curie temperature of a 55% alloy is in the vicinity of 60°K so that the hfs should be within a few percent of its 0°K value at the temperature of measurement. The zero value reported for the field means that the time-average field at the iron nucleus has become zero, i.e., that the iron spins are no longer aligned by the ferromagnetic alloy system; it does not indicate that the d shell of the iron has become filled. This conclusion is dictated by the small change observed in the isomer shift in this range of composition.

The observed decrease in the magnitude of the field at the iron nucleus between 0 and 40% copper is only 9% compared to a 67% decrease in the magnetization of the alloy. This is in agreement with the relative stability of the atomic configuration of iron found in the discussion of the isomer shift. This stability arises from the splitting-off of discrete states from the 3d band of the alloy caused by the difference in charge between iron and copper. The discussion is analogous to that given by Slater¹¹ for chromium in nickel, where it is pointed out that an impurity atom whose charge differs by more than two units from that of the host lattice will result in split-off levels. These fall above the band if the impurity atom has a smaller charge than the lattice, as does iron in copper. One level per atom apparently lies sufficiently high so that it remains above the Fermi level even in pure copper and is consequently largely unoccupied. However, small changes in the occupancy of this state can be produced by the motion of the Fermi level, and it is possible that this accounts in part for the observed changes in the isomer shift and in the field at the nucleus.

A detailed interpretation of these changes cannot be given, however, since the field at the nucleus includes contributions from a number of other sources such as

¹¹ J. C. Slater in *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, pp. 1-136.

the conduction electron polarization, whose magnitude has not yet been established.

LINEWIDTH

The linewidth of the absorption for the copper-rich alloys was found to be a strong function of composition. It is smallest in pure Cu and largest in the middle of the composition range, Fig. 1. The measured linewidths are made up of the following contributions: (1) the natural linewidth of the absorber, (2) the finite thickness broadening of the absorber, (3) instrumental broadening including a small amount of geometric broadening, (4) the natural linewidth of the source, and (5) extranuclear effects in the alloy. The first four are the same for all the alloys studied; the last one exhibits the composition-dependence under discussion, and is the only one which changes from alloy to alloy.

Composition-dependent broadening could arise from the range of environments experienced by various Fe atoms in the alloy, i.e., inhomogeneous isomer shift broadening. The fact that the smallest linewidth was obtained in pure metal and that the linewidth did not exhibit a significant temperature dependence is in accord with this interpretation. However, since the observed broadening is almost as large as the total isomer shift between the nickel and copper environments, it is doubtful that this mechanism can account for the entire effect. Moreover, it cannot explain the rapid change of linewidth with small nickel admixture.

Broadening could also arise from the magnetic hyperfine and quadrupole interactions. Magnetic broadening, especially in the midrange alloys, would exhibit a strong temperature dependence related to the spin relaxation time. No such effect was found; the linewidth was independent of temperature even in the ferromagnetic 55% Cu alloy. Quadrupolar broadening could arise in these cubic alloys without lattice distortion through the Kohn-Vosko¹² effect, i.e., from the spatial charge density fluctuations around an impurity atom. These produce electric field gradients which can interact with the quadrupole moment of the $I=\frac{5}{2}$, first excited state of Fe⁵⁷. The rapid increase of linewidth produced by small Ni admixture suggests that this effect is operative since the charge density fluctuations around a single impurity atom extend its influence over a considerable volume.

A numerical estimate of the magnitude of this effect may be made on the basis of the computed field

gradients¹² in the vicinity of an impurity bearing unit charge. Although the computed values were obtained for Mg, Zn, and Cd it has been pointed out¹³ that the effect of Ni on the Cu NMR is very similar in magnitude to that of Mg, Zn, or Cd. Using the known quadrupole moment for the first excited state of Fe⁵⁷,¹⁴ we obtain for the 12 positions in the first shell surrounding the impurity a quadrupole splitting, $\frac{1}{2}e^2qQ$, of 0.011 cm/sec; for the 6 in the second shell, 0.005 cm/sec; and for the 24 in the third shell, 0.003 cm/sec. These numbers may be compared with a broadening of 0.004 cm/sec in a 2% Ni alloy and 0.007 cm/sec in a 5% Ni alloy. It is clear that at low Ni concentration this effect readily accounts for the observed broadening. It is certainly not applicable to the midrange composition alloys where the first mechanism discussed may make an important contribution.

It is also of interest to ask what the effect of such quadrupole splitting is on the magnetic hfs observed in the nickel-rich alloys. It may be shown that when a suitable average has been taken over the random angle between the direction of the magnetization and the axis of the electric field gradient tensor, the major effect is the broadening of the absorption lines; the displacement of the lines is much smaller than the precision of the measurement, which is $\pm 1\%$.

CONCLUSIONS

The Mössbauer effect of Fe⁵⁷ in Cu-Ni indicates that the atomic configuration of iron in these alloys remains very similar to that of metallic iron. This is consistent with the paramagnetic behavior of iron in copper, known from earlier measurements, and can be accounted for by assuming that the presence of iron atoms causes discrete levels to split off from the d band of the alloy. Changes in the linewidth in the copper-rich alloys are ascribed to quadrupole splitting of the first excited state of Fe⁵⁷ produced by the electric field gradients in the vicinity of nickel atoms.

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¹² W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).