

tween these two extremes as expected. However, the experimental peak appears to be narrower than expected and also the Macek theory predicts a cross section that is too large for lower energies and too small for the higher energies even when the experimental uncertainty of 30% is taken into account. The Born results are too low by a factor of 20.

The peak was also observed using other projectiles and other target gases. It is reasonable to expect that the effect would be appreciable in emulsions and might be useful in explaining the difference in the energy-loss rates of the positive and negative pions.⁶

This experiment provides the first conclusive evidence that charge exchange into continuum states is an important mechanism of ionization by ion impact. Furthermore, in contrast to earlier speculations,⁹ these results show that the Faddeev equations, which provide a natural means of formulating this mechanism in a theory, may apply to the electrostatic interaction.

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Hyperfine Interactions of Fe⁵⁷ in a Frozen Argon Matrix*

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We describe technique for the isolation and observation of iron atoms frozen into a rare-gas matrix. A large quadrupole interaction points to the existence of a stable iron molecule (Fe₂) in an argon matrix at $T = 4.2^\circ\text{K}$.

For a decade now, the Mössbauer effect has been used to investigate the hyperfine interactions of Fe⁵⁷ in a great variety of materials. During this time, however, little effort has been concentrated on isolating and observing iron particles which consist of a few atoms only. In view of the paucity of data on such systems we have constructed an apparatus which uses the principle of matrix isolation¹ as developed by optical spectroscopists. Here an absorber is created which consists of many small aggregates of atoms that can be studied with the Mössbauer effect. The object of this communication is to describe briefly the technique (which will be reported fully elsewhere) and report the first results that we have obtained with its use.

The purpose of the instrumentation is to generate an atomic beam of iron. It is subsequently trapped, atom by atom, in a simultaneously pro-

duced frozen rare-gas matrix, which allows isolation of the iron with negligible crystal-field interactions. A schematic plan diagram of the experimental layout is shown in Fig. 1. Iron metal powder enriched to 70% Fe⁵⁷ is loaded into an alumina crucible which in turn is placed in a tantalum furnace *F* which can be electrically heated to a maximum temperature $\approx 1400^\circ\text{C}$. The furnace housing *H* is attached to the side of a liquid helium cryostat so that Fe which evaporates from the crucible can be condensed onto a Be disk *B* suspended from the bottom of the liquid-He⁴ bath. The geometry of the furnace and cryostat produces a collimated beam of evaporated iron atoms with a diameter ≈ 2 cm at the Be disk which is situated 10 cm from the mouth of the alumina crucible. Data on the absorber which is formed from the atomic beam are collected with a conventional constant-acceleration Möss-

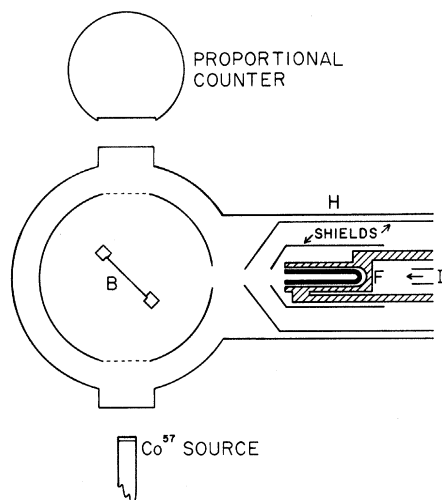


FIG. 1. Schematic of the apparatus used for depositing iron and rare gas onto a cold substrate. It shows also how the Mössbauer effect measurement is taken.

bauer spectrometer.

In order to isolate individual Fe atoms, or groups of Fe atoms, a stream of a rare gas with an adjustable flow enters through *I*. It condenses on the Be disk which is cooled to 4.2°K. The rare-gas-to-iron atomic ratio is controlled by manipulating the furnace temperature and/or the gas flow rate. When the absorber is being laid down the radiative thermal loading on the Be disk does not noticeably affect the rate of accretion of rare gas (except neon) until ≈ 5 mg/cm² has been deposited. For greater matrix thicknesses the rate gradually drops; therefore, in our experiments all absorbers consist of no more than 5 mg/cm² of rare gas.

It takes approximately three hours to build up an absorber and the rare-gas accretion on the Be disk is continuously monitored by measuring the attenuation of the iron 6.4-keV *K* x ray from a Co^{57} -in-Cu source. It is not possible to measure simultaneously the deposition rate of the iron. This was carried out in a separate experiment where a known weight of iron was evaporated and the collection efficiency of the Be disk was determined from a Mössbauer-effect measurement. The major problems here are that the absorber thickness varies because of geometrical considerations and the *f* factor of the Fe-metal absorber formed in this manner is unknown. Furthermore, appreciable scattering of Fe atoms out of the beam may be taking place when the rare gas is added to the system. This last problem will be somewhat ameliorated with an improvement which will allow gas to be added

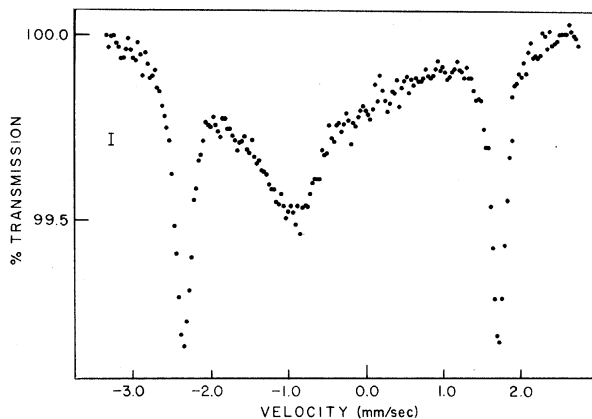


FIG. 2. Mössbauer spectrum of Fe^{57} atoms dissolved in a frozen argon matrix at $T = 4.2^\circ K$.

external to the furnace area. Thus the uncertainty of about 50% in the iron deposition rate is the main source of error in the rare gas/iron atomic ratios.

In our initial experiments argon was used as the solvent matrix for the iron atoms. Figure 2 shows the Mössbauer spectrum of Fe^{57} in solid Ar at $T = 4.2^\circ K$ using a source of Co^{57} in Pd. The absorber consists of 3.0 mg/cm² of Ar and approximately 0.07 mg/cm² of Fe^{57} , giving a ratio Ar/Fe ≈ 40 , or Ar/ $Fe^{57} \approx 60$.

The spectrum has two completely dissimilar features, which are (1) two narrow peaks with a separation of 4.06 ± 0.03 mm/sec, an isomer shift with respect to iron metal (at $T = 300^\circ K$) of -0.136 ± 0.006 mm/sec, and a peak linewidth (corrected for instrumental broadening) of 0.22 ± 0.02 mm/sec; (2) a central region in which there is a very broad feature indicative of more than one line. This division of the spectrum into two separate parts is supported by the results of other experiments with different Ar/Fe ratios in which the two components do not maintain a constant relative amplitude. Further experiments are in progress to improve delineation of the central feature in order to aid in its interpretation.

At $T = 4.2^\circ K$ solid Ar is a fcc crystal with a lattice parameter $a = 5.312 \text{ \AA}$ and a nearest-neighbor distance $a/\sqrt{2} = 3.76 \text{ \AA}$. If the iron atoms are distributed randomly in substitutional sites in the argon matrix, the probability of an iron atom having as one of its twelve nearest neighbors another iron atom is 23%. Because of the existence of this considerable percentage of pairs of iron atoms on adjacent lattice sites, we assign the two narrow peaks in the spectrum to the quad-

rupole splitting produced by a proposed Fe-Fe "molecule" (dimer). Such a molecular configuration could have a strong overlap of the iron $3d$ orbitals along its symmetry axis and thus give rise to a large electric field gradient (EFG) at the iron nucleus. In fact, the quadrupole splitting is approximately 10% larger than the previous largest value reported by Johnson, Marshall, and Perlow² for the compound $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$. Our value of 4.06 mm/sec agrees with the calculation by Ingalls³ for the magnitude (4.1 ± 0.2 mm/sec) of the bare quadrupole-coupling constant of the $3d^6$ configuration without a lattice contribution to the EFG.

The quadrupole-interaction linewidths indicate that the effects of one iron dimer on another can be neglected since there is no appreciable line broadening above the natural linewidth value.

Therefore, each dimer can be considered as an isolated entity without external contributions to the EFG.

It is not possible to obtain an accurate value for the Mössbauer fraction f for the dimer in view of the uncertainty associated with determining the iron concentration. However, a rough estimate indicates that $f \approx 0.2$.

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Reply to "Longitudinal Diffusion Coefficients Misnamed," by R. N. Varney*

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Varney has recently applied random-walk methods to discuss the longitudinal diffusion of gaseous ions drifting in an electric field, and he obtained results which differ from those obtained by solution of the diffusion equation. Varney's analysis leads him to state that the measured longitudinal diffusion coefficients are not diffusion coefficients at all. Several arguments are presented here to refute Varney's findings.

In a recent Letter,¹ Varney has obtained a relation between the longitudinal diffusion coefficient D_L for gaseous ions in an electric field E , and their drift velocity v as measured in a drift-tube experiment, by comparing random-walk theory and diffusion theory. Since these are equivalent descriptions of the same physical phenomenon, such a relation should exist, and indeed the Einstein relation² for thermal-energy ions is well known. It states that $D_L \propto K$, the mobility, where $K = v/E$. This relation implies that $D_L \propto v$ if E is held constant. However, Varney obtains a different relation, with $D_L \propto v^2$, without specification of the ionic energy, and he attempts to resolve the incompatibility with the Einstein relation by assuming a physical distinction between diffusion and random-walk phenomena. Furthermore, he purports to show that our measured values³⁻⁶ of D_L are not diffusion coefficients at all.

In this Letter we wish to make three points. Firstly, random-walk theory and diffusion theory are descriptions of the same physical process;

secondly, Eq. (1) of Varney's Letter, $\Delta t/t \propto n^{-1/2}$, is inappropriate; and thirdly, there are approximations in diffusion theory which Varney has not taken into account.

The first point is basic to kinetic theory and need not be discussed further here.⁷ Now as regards the second point. In Varney's first equation, t is the average drift time, and Δt is the half-width of the ionic transit time distribution for constant n and might more appropriately be called Δt_n . Experimentally the measured quantity is the time for an ion to drift a given distance from the source, whereas Varney's first equation applies to the time it takes for the ion to make n collisions. Further, we can show that these are not the same, at least for drift velocities small compared with the total ion velocity. Rather than $\Delta t_n/t$, let us consider $\Delta x/s$, where Δx is the rms variation in position and s the total distance traveled. Then we have

$$\Delta x/s = n^{-1/2}. \quad (1)$$