Mössbauer Effect at High Pressure for Fe⁵⁷ in Titanium, Vanadium, and Copper*

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We have measured the effect of pressure to 250 kbar on the isomer shift of Fe⁵⁷ in dilute solution in titanium, vanadium, and copper. These results and previously published data on Fe⁵⁷ in iron indicate that for the bcc metals of the first transition-metal series, the 4s-electron density scales approximately with bulk density. For more closely packed phases the s-electron density changes less rapidly than the bulk density.

I. INTRODUCTION

RECENTLY, Mössbauer experiments with Fe⁵⁷ in iron at high pressure have been done by Pound et al.[1] Nicol and Jura,[2] and by Pipkorn et al.[3] The isomer-shift data obtained by these authors for the body-centered-cubic (bcc) phase of iron indicate that for a change in lattice parameter up to 2% the only effect of the applied pressure is to scale the Fe⁵⁷ 4s-electron density proportional to the bulk density without affecting the 3d electrons. The experiments reported here show that the same behavior is found for a solid solution of Fe⁵⁷ in bcc vanadium, whereas the solid solutions of Fe⁵⁷ in titanium and in copper show a more complicated behavior.

The isomer shift ϵ is defined as the difference in energy between the centers of gravity of the emission and of absorption lines.[4] It is here expressed in terms of the Doppler velocity at resonance measured with a stainless steel absorber. As pointed out by Pound et al.[1] The pressure coefficient of the isomer shift consists of a small contribution arising from the change in vibrational energy, which will be neglected, and of a term arising from the change in electron density at the Fe⁵⁷ nucleus,

$$\left(\frac{\partial \epsilon}{\partial p}\right)_T = \text{const}\left(\frac{\partial \psi(0)^2}{\partial (V/V_0)}\right)_T \left(\frac{\partial (V/V_0)}{\partial p}\right)_T. \quad (1)$$

Walker, Wertheim, and Jaccarino[4] have given a relationship between isomer shift and electron density. With their sign convention an increase in s-electron density corresponds to a decrease in isomer shift. If the electron density scales with volume V, the isomer shift due to the 4s electrons only will vary as[3]

$$\frac{\partial \epsilon}{\partial (V/V_0)} = 0.14 \text{ cm/sec}. \quad (2)$$

II. EXPERIMENT

The method of source preparation was essentially identical with that described by Pipkorn et al.[3] Radioactive Co⁵⁷ was introduced into small foils of the sample metal by plating and diffusion. In all cases the concentration of Co⁵⁷ plus carrier was less than 1%. The absorber used was the same stainless steel foil enriched in Fe⁵⁷ used in the work on iron. The high-pressure cell and Mössbauer spectrometer are also described in detail by Pipkorn et al.[3] The isomer shifts were obtained by computer from a least-squares analysis of the experimental Mössbauer spectra.

III. RESULTS

The isomer shifts at zero pressure for Fe⁵⁷ in the three host metals used in this study are listed in Table I.[5]

TABLE I. Atmospheric-pressure isomer shift for Fe⁵⁷ in various transition metals—relative to stainless steel absorber.

Metal	ϵ_0(cm/sec)
Ti	-0.0110 ± 0.0004
V	-0.0155 ± 0.0003
Fe	$+0.0086 \pm 0.0005$
Cu	$+0.029 \pm <0.001$

For comparison we also give the isomer shift at zero pressure relative to the same absorber for Fe⁵⁷ in iron.[3] Figure 1 shows the isomer shift versus pressure for Fe⁵⁷ in copper, titanium, and vanadium. Copper crystallizes in the face centered cubic (fcc) structure. Titanium is hexagonal close packed (hcp) at low pressure, but near 80-85 kbars it transforms (quite sluggishly) to a distorted cubic structure.[6] Vanadium crystallizes in the bcc structure as does iron below 130 kbar. At higher pressures iron assumes the hcp structure.

Figures 2 and 3 show the isomer shifts versus fractional volume change for the three host lattices plus that for pure iron. For iron the density data of Clendenen

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