

## Low-temperature phase transition and isomer-shift systematics in intermediate phases of rare-earth-gold compounds\*

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The temperature dependence of the  $^{197}\text{Au}$ ,  $^{166}\text{Er}$ , and  $^{169}\text{Tm}$  Mössbauer effect has been studied in intermediate phases of  $RAu$  ( $R = \text{Sc, Ho, Er, Tm, Yb, Lu}$ ) with the CsCl structure. Our results indicate that the CsCl structure is metastable and undergoes a low-temperature martensitic phase transformation to a close-packed (FeB-like) structure. The ratio of the quantity of the two phases present at 4.2°K for various compounds is obtained. Mössbauer-absorption patterns for  $^{166}\text{Er}$  in  $\text{ErAu}$  have a temperature dependence which is characteristic of relaxation effects. Isomer-shift systematics for  $^{197}\text{Au}$  in  $RAu$  for the CsCl and the transformed close-packed phases are discussed.

A systematic study of  $RAu$  ( $R = \text{Sc, Ho, Er, Tm, Yb, Lu}$ ) with the CsCl structure was undertaken by means of Mössbauer spectroscopy.<sup>1-3</sup> The initial purpose of the investigation was to examine magnetic properties and possible charge-transfer effects in binary intermediate phases containing a rare-earth element. Our results show that the CsCl structure in these intermetallic compounds is metastable and that at low temperature a martensitic transformation takes place which at equilibrium leads to a two-phase system. Moreover, the ratio of the quantity of the phases at a given temperature is dependent on the thermal history of the alloy. We note that these results may alter somewhat the interpretation of previous physical measurements (resistivity,<sup>4</sup> susceptibility<sup>5,6</sup>) in which the assumption was made that the room-temperature phase (CsCl) was stable at low temperature.

Kissell and Wallace have made susceptibility measurements for  $RAu$  compounds ( $R$  is a lanthanide) of the CsCl structure.<sup>5</sup> Néel points were observed only in compounds of Au with Gd, Tb, and Ho with transition temperatures in the range from 43°K for TbAu to 10°K for HoAu. The effective moments (except for Yb) were found to be approximately those of the free tripositive lanthanide ion. Susceptibility peaks were not observed for compounds of Au with Dy, Er, Tm, or Yb. Electrical-resistivity measurements by Chao and Duwez<sup>4</sup> indicate a magnetic-transition temperature for HoAu [(13–16)°K], for ErAu [(13–19)°K], and for TmAu [(8–19)°K]. All transitions are paramagnetic to antiferromagnetic.

Much discussion has been devoted to the possibility of charge transfer in metallic compounds<sup>6</sup>

and in particular to transfer of charge to the Au atom in both solid solution and intermediate phases. Early Mössbauer isomer-shift measurements were discussed in terms of charge transfer to the more electronegative Au atom based on observations that isomer-shift measurements indicated a substantial increase in the  $s$  density in the vicinity of the Au nucleus.<sup>7,8</sup> Similar conclusions have been reached on the basis of solubility limits of Au in solid solutions.<sup>9</sup> More recent photoemission results by Watson *et al.*<sup>10</sup> and Friedman *et al.*<sup>11</sup> tend to indicate that there is little net charge flow to the Au atom, but that the increase of non- $d$  conduction-electron count at Au sites is compensated by a decrease in the number of  $5d$  electrons. This latter possibility was suggested by Barrett *et al.*<sup>8</sup> to explain the isomer-shift results in  $\text{AuAl}_2$ .

In the following we present a Mössbauer-effect study which indicates that, in equiatomic intermediate phases of rare earth and gold, a martensitic transition takes place from CsCl to a close-packed structure. At low temperatures, a two-phase system is obtained. Hyperfine parameters are obtained for Au in both component phases; the variation of the isomer shift as one changes the rare earth is discussed.

### EXPERIMENTAL

The alloys were prepared by arc melting 99.99% pure rare earth with 99.99% pure gold. The heat treatment necessary to retain the cubic phase (~95%) at room temperature varied with the compound. For example, HoAu is a compound which has a high temperature transformation and was quenched from above the transformation temperature to retain the CsCl structure. All samples

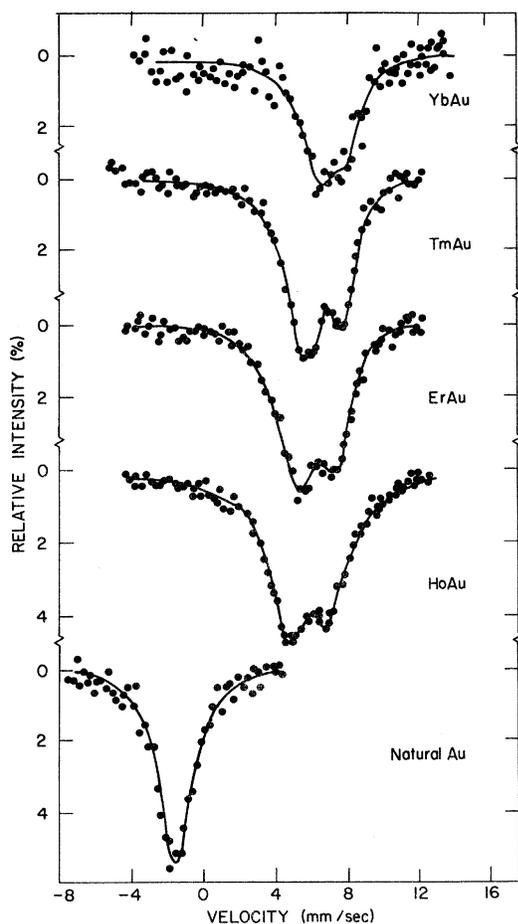


FIG. 1. Mössbauer-absorption patterns for  $^{197}\text{Au}$  in RAu at 4.2 °K relative to  $^{197}\text{Au}$  in Pt.

were examined by both metallographic methods and x-ray techniques. Before cooling to low temperatures, the small amount of second phase is of the  $\text{MoSi}_2$  type in ScAu, YbAu, and LuAu; and TmAu. Superlattice lines of the CsCl phase are difficult to observe because of the proximity of Au to the rare earths in the periodic chart. However, careful examination of Debye-Scherrer patterns disclosed the CsCl superlattice to be present in HoAu (relatively strong), TmAu (weak), ErAu (weak), and ScAu (strong).

A conventional Mössbauer spectrometer was used in the time mode. Spectra of the 77.3-keV resonance in  $^{197}\text{Au}$  were obtained using a foil of  $^{197}\text{Pt}$  as source. In addition, a limited number of spectra were obtained for the 80-keV resonance in  $^{166}\text{Er}$  (source of 10-wt% Ho in Al), the 8.4-keV resonance in  $^{169}\text{Tm}$  (source of 10-wt% Er in Al), and the 66.7-keV resonance in  $^{171}\text{Yb}$  (source of  $\text{TmAl}_2$ ). An important feature of the Au, Er, and Yb cases is that the Mössbauer fraction decreases rapidly with increasing temperature and experiments are limited to temperatures of  $\sim 100^\circ\text{K}$  or below.<sup>12</sup> This latter

fact is important for those systems which may have high magnetic-transition temperatures.

#### RESULTS AND DISCUSSION

The  $^{166}\text{Er}$  Mössbauer effect in ErAu was examined from 4.2 to 80 °K. Below 10 °K, the spectrum showed a simple five-line pattern characteristic of a magnetic splitting. The hyperfine field observed was  $8300 \pm 200$  kOe, very near the free-ion value of 8100 kOe.<sup>13</sup> This is essentially in agreement with the fact that the paramagnetic moment in this material is very near the Er free-ion moment.<sup>5</sup> As the temperature is increased, one sees an enhancement of intensity near the center of the pattern, followed by a collapse of the hyperfine pattern into a broad single line. Such behavior is characteristic of situations in which the electronic relaxation time is comparable with the nuclear Larmor frequency ( $\approx 10^{-8}$  sec).<sup>14</sup> Because of the presence of these relaxation effects, discussion of possible magnetic transitions becomes difficult.

At room temperature, the hyperfine spectrum of  $^{169}\text{Tm}$  in TmAu consists of a single line which is 1.5 times broader than the narrowest linewidths available from our source. As the temperature is lowered, the line slowly broadens, becoming about 3 times the natural width at 78 °K, and showing widely split, but poorly resolved, structure at 4.2 °K. This again is typical of paramagnetic relaxation effects. One may note that the magnetic measurements of Kissel and Wallace indicate that TmAu is not magnetically ordered at this temperature. This is not in conflict with the present measurements.

At 4.2 °K, the spectrum of  $^{171}\text{Yb}$  shows a single unsplit line, indicating no magnetic order at this temperature. We are not able to determine the charge state of Yb in YbAu because the isomer shift is very insensitive to the changes in valence state. However, we note that the absence of any magnetic splitting in the Yb resonance, together with the large lattice parameter tends to corroborate the conclusion of Kissel and Wallace that the  $2^+$  state is predominant.

Absorption spectra for  $^{197}\text{Au}$  in several of these compounds at 4.2 °K are shown in Fig. 1 and a typical temperature dependence is shown in Fig. 2. For this isotope, the observed splitting could be interpreted as being due to either a magnetic or electric quadrupole hyperfine interaction, if not a combination of both. There is a marked asymmetry present in these spectra. However, the cubic point symmetry for the Au site in the CsCl structure should preclude the presence of a quadrupole interaction and one is inclined to discuss the spectra in terms of a pure magnetic hyperfine splitting. In addition to the problem of asymmetry the spectra are found to remain essentially unchanged to temperatures much higher than the magnetic-transition

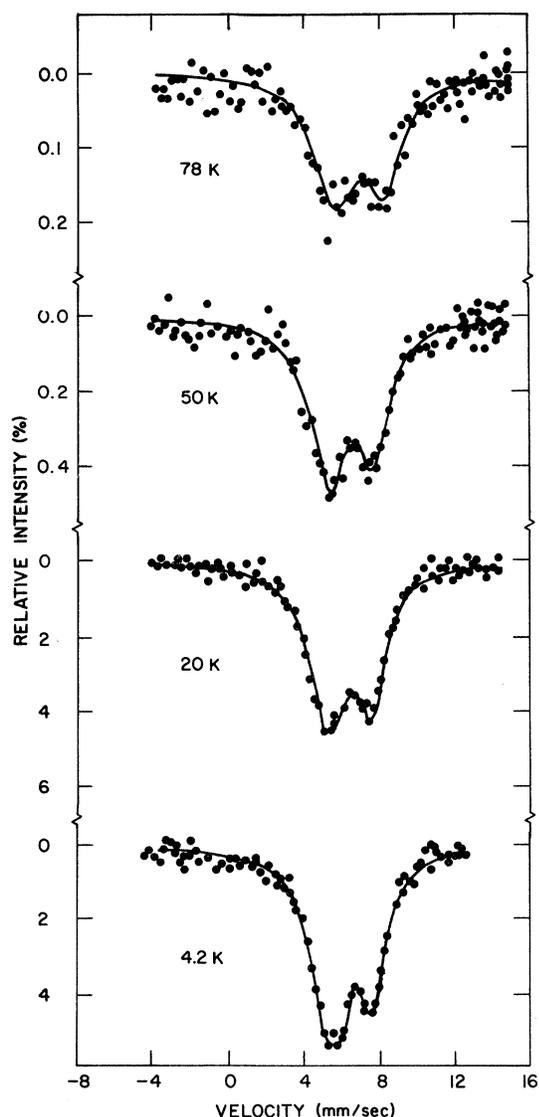


FIG. 2. Temperature dependence of the Mössbauer absorption of  $^{197}\text{Au}$  in TmAu.

temperatures quoted by Kissell and Wallace<sup>5</sup> and Chao and Duwez.<sup>4</sup> This could be due to slow electronic relaxation as in the rare-earth spectra discussed above; however, such phenomena are less probable in metallic systems and have not been previously seen in  $^{197}\text{Au}$  spectroscopy in any type of crystal system. Consequently, we were led to a conclusion which results in a sample that contains CsCl plus a noncubic phase. The latter will give a symmetric doublet in the absence of magnetic interactions; the former will give a single line. If these two phases are isomer shifted slightly relative to the one another, the resulting spectrum will have the observed asymmetric appearance. Analysis of the data with these assumptions allows a determination of the relative amounts of each phase.

The postulate of such a phase transformation has been verified by x-ray diffraction at low temperature by Barrett and Mueller<sup>15</sup> who find hysteresislike behavior characteristic of that found in martensitic transitions from the CsCl structure. Martensitic transformations take place over a range of temperature with the volume of the transforming phases increasing rapidly as the temperature decreases. In thermal cycling, curves of the fraction of a given phase versus temperature form hysteresislike patterns with the equilibrium state at both high and low temperature often a mixed state. The low-temperature phase in the *RAu* compounds studied here is structurally similar to FeB (hereafter referred to as FeB-like) but has not been fully characterized. At room temperature, after the temperature has been lowered from that of the anneal, the alloys are principally in the CsCl-type structure. However, as the temperature is reduced to  $\sim 100^\circ\text{K}$ , there is a transformation to principally the FeB-like structure; only small further changes take place as the temperature is reduced to  $4.2^\circ\text{K}$ . Moreover, upon warming to room temperature, the low-temperature phase is largely retained. The Mössbauer pattern for  $^{197}\text{Au}$  in HoAu for a single-phase compound subsequently prepared in the low-temperature structure is shown in Fig. 3. In the FeB structure, the coordination of the Au atom is ten (four Au and six rare earths at various distances), with each Au atom in a similar environment. In the absence of magnetic splitting, a symmetric quadrupolar doublet is expected for the Mössbauer pattern, as observed. One should contrast this expectation with Fig. 1, where the strongly asymmetric pattern shown is due to the superposition of the quadrupole doublet due to the low-temperature phase and the single line due to the non-transformed material with the CsCl structure.

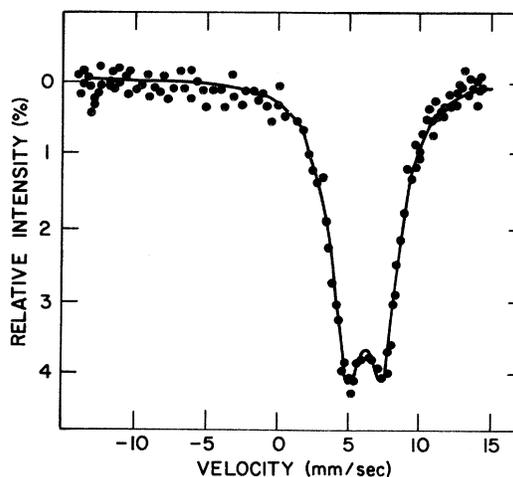


FIG. 3. Absorption pattern for FeB-like HoAu at  $4.2^\circ\text{K}$ .

TABLE I. Isomer shift relative to  $^{197}\text{Au}$  in gold at 4.2 °K for both FeB-like and CsCl phases is given, as well as the quadrupolar splitting and width for two-line fits to doublet-absorption patterns. The widths for CsCl patterns are 2.2 mm/sec. The ratio of the quantity of CsCl and FeB-like phases at 4.2 °K is tabulated for HoAu, ErAu, and TmAu.

Compound	Crystal type	Isomer shift (mm/sec)	$E_Q$ (mm/sec)	Width (mm/sec)	CsCl/FeB-like
HoAu	FeB-like	+7.46 ± 0.07	4.87 ± 0.05	2.46 ± 0.05	
ErAu	FeB-like	+7.48	4.93	2.40	
TmAu	FeB-like	+7.58	4.36	2.30	
ScAu	CsCl	+6.21		2.20	
HoAu	CsCl	+7.05			0.10
ErAu	CsCl	+7.10			0.10
TmAu	CsCl	+6.51			0.16
YbAu	CsCl	+7.35			
LuAu	CsCl	+6.66			

Magnetic interactions in  $^{197}\text{Au}$  spectra can cause line broadening of the doublet, plus an asymmetry in the intensities. If present here, however, the magnetic hyperfine field must be very small.

The Mössbauer determinations at 4.2 °K of the ratio of the quantity of CsCl to FeB-like phases (assuming the Debye temperature is approximately the same in both phases and taking a pure quadrupole pattern for the latter phase) are shown in Table I. The Mössbauer parameters for both the high-temperature CsCl and low-temperature FeB-like phases are also shown in Table I. The corrections to the isomer shift which arise from interference effects are small (0.01 to 0.02 mm/sec).<sup>16</sup>

The isomer shift is sensitive to the volume-related change in charge density, as well as the change in valence-electron character (hybridization), and scales nonlinearly with volume changes.<sup>17</sup> In the intermetallic compounds studied here the electron/atom ratio is the same for each  $RAu$  system but there is, due to the lanthanide contractions, a systematic variation in the density of valence electrons/unit volume. Since near neighbors are of different type in the CsCl structure, it is only possible to determine the sum of the atomic vol-

umes of the individual constituents.<sup>18</sup> Thus, it is not possible to separate the shift components due to the change in atomic volume and to the change in  $d$  hybridization. The change in shift from Ho to Tm in the  $RAu$  CsCl-type compounds is opposite to that expected from the volume change of the unit cell alone; either the volume of the Au atom must increase as the rare-earth ion becomes small and (or) the degree of hybridization must decrease.

In summary, the rare-earth-gold equiatomic intermediate phase is metastable, transforming from principally CsCl-type at room temperature to principally a close-packed structure at low temperature with a strong hysteresis effect present. In view of this, various physical measurements, such as susceptibility and resistivity, made to low temperature and discussed on the assumption that the CsCl-type structure was stable, may have to be reinterpreted. The isomer-shift systematics in the CsCl-type structures cannot be interpreted in detail because volume and hybridization effects cannot be separated. The charge density at Au nuclei is larger in the transformed FeB-like phases and is almost independent of the identity of the rare earth.

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