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**Authors:** Nicholas DeCristofaro and Roy Kaplow

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Nicholas DeCristofaro and Roy Kaplow
Massachusetts Institute of Technology

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Loss of Lattice Rigidity in Austenite

Nicholas DeCristofaro† and Roy Kaplow‡‡

Mössbauer spectra were taken at and below room temperature in iron-2.4 wt.% nitrogen samples containing various amounts of stabilized martensite and austenite (Mₜ = 260K). The intensities of the martensite spectra increase with decreasing temperature as expected from the normal thermal variation of the recoilless fraction. Conversely, the intensities of the austenite spectra are smaller below room temperature and Mₜ, and decrease with decreasing temperature. This corresponds to a decreasing recoilless fraction, which is associated with a lessening of lattice resistance to excitations caused by the transference of the gamma-ray recoil momentum. This behavior is thought to be related to lattice instabilities in the austenite phase, possibly related to its transformation to martensite. The magnitude of the effect indicates that, although the excitations in themselves may be localized, these instabilities are characteristic of the bulk material and cannot be explained in terms of the conventional theory of pre-existing martensitic embryos.

I. Introduction

Recently, the concept that various crystal lattices become structurally unstable on cooling has assumed an important role in models for martensitic or displacive transformations. In this context, a number of anomalous effects occurring in the parent (austenite) phase at temperatures above Mₜ have been reported. Electron microscopic effects [1-5], softening of elastic constants [6,7], and resistivity and magnetic anomalies [8,9] have been observed. Mössbauer studies of Fe-Ni and Co-Fe systems [10-12] show a decrease in the recoilless fraction of the parent phase as the temperature is lowered to Mₜ. It has been argued that these "premartensitic phenomena" intensify as the temperature is lowered to Mₜ [1] and continues to exist in the retained austenite at temperatures below Mₜ [13].

These effects have been associated with the martensitic transformation in a variety of ways. Models exist in which specific phonon modes in the parent phase related to the martensitic structure [14,15] become unstable and eventually trigger the transformation through their own stress fields [16-18]. Other interpretations speculate two step processes including either the slight distortion of the parent lattice [5] or the precipitation of a transitory phase [3,4] preceding the actual transformation. In many instances, the model for martensitic trans-
formation involves inhomogeneously distributed "embryos" based on (a) spatially localized, "soft" vibrational modes [19], (b) static atomic displacement waves [10], or (c) particular configurations of defects (e.g. dislocations) [21].

II. Experimental Procedure

Samples of iron 2.4 wt.% nitrogen (8.9 at.%) austenite (M, approximately 260°C) [22] were produced by nitriding iron foil (0.025 mm thick) in flowing mixtures of NH₃ and H₂ at 973°C and rapidly quenching directly from the nitriding atmosphere.

Mössbauer spectra were measured on a constant acceleration spectrometer with a gamma-ray source of ⁵⁷Co embedded in a copper matrix. The austenite absorber was mounted in a low-temperature dewar on this spectrometer so that its temperature could be controlled in situ, without disturbing the source-sample-detector geometry.

The austenitic sample was cycled a number of times between room temperature (295°C) and 183°C. The total time spent at 183°C exceeded 24 hours and the total time at room temperature following the first quench exceeded one week. This process served to ensure that the martensite formed was stabilized both in amount and with respect to short term room temperature aging for this temperature range. The first data set, following this treatment, comprised a sequence of Mössbauer measurements at 295, 183 and 295°C. The spectrum recorded at room temperature is illustrated in Figure 1; it indicates the presence of approximately 40% martensite (the complex, spectrum labeled M), and 60% austenite, (the spectrum labeled A).

The sample was then quenched to 82°C and cycled between this temperature and room temperature in a manner similar to that described above. Following this treatment, another series of Mössbauer spectra were recorded at 295, 183, 82 and 295°C. The spectrum measured at room temperature indicated that during the additional cooling from 183°C to 82°C, the amount of martensite increased to approximately 55%.

III. Analysis of Mössbauer Spectra

The recoilless fraction, which determines the absolute magnitude of the relevant spectra, is related to a recoil energy, R, that would be transferred to a single free and motionless atom when its nucleus absorbs a gamma-ray, and to the effective, quantized energy increment for available lattice excitations, E*, in the form: [23]

\[ f_T = \exp \left(-\frac{R}{E^*}\right) \]  

(1)

For the vibrational excitation of a Debye solid:

\[ E^* = \left(\frac{1}{6}\right) k_B \theta_D \frac{1}{1/4 + (T/\theta_D)^2} \int_0^{\theta_D/T} \frac{x^2}{e^x - 1} dx \]  

(2)
where $k_B$ is Boltzmann's constant, $\Theta_D$ the Debye characteristic temperature, and $T$ the absolute temperature. On the basis of ordinary temperature-dependent vibrational behavior, the recoilless fraction should increase with decreasing temperature. This temperature dependence, expressed in terms of $f_r / f_{295}$, predicted by Equation (1) and (2), is illustrated as the solid curve in Figure 2. The value of $\Theta_D \approx 411^\circ K$, taken as an average and from interpolation and extrapolation of various data [24,25] is appropriate for both phases.

The theoretical intensity of a Mössbauer absorption peak, $P_{th}(E_s)$, is related to the recoilless fraction, $f_T$, through the convolution: [26]

$$P_{th}(E_s) = \int_{-\infty}^{\infty} I(E, E_s) \left[1 - \exp \left(-f_T n \sigma(E)\right)\right]$$  (3)

where $I(E, E_s)$ is the nominally Lorentzian energy distribution of the gamma-ray source, $n$ is the effective thickness of the absorber in nuclei per cm$^2$, and $\sigma(E)$ is the cross section for resonant absorption. In practice, the proper absorption intensities and shapes are obtained through the convolution of the theoretical intensity with a Gaussian curve to compensate for instrumental broadening [17]. Since the nuclear parameters are constant, the temperature variation of the magnitude of resonant absorption in each phase is dependent only on $f_T$.

When the argument of the exponential term in Equation (3) is small, the depth of the Mössbauer peaks is also small and may be approximated as being directly proportional to $f_T$. This is the case for the ferromagnetic martensite spectra. For the austenite spectrum, where the exponent is larger, the more rigorous nonlinear treatment of Equation (3) must be applied.

IV. Experimental Results

The first series of Mössbauer measurements, on 40% martensite stabilized at 183$^\circ K$, were recorded at 295, 183 and 295$^\circ K$ again. The martensite peaks showed increased intensity at the low temperature by the amount expected from the thermal increase in $f_T$. The austenite peak, however, showed a decrease in intensity corresponding to a decrease in $f_T$ of approximately 9%.

The second series of measurements, on 55% martensite stabilized at 82$^\circ K$, were recorded at 295, 183, 82 and 295$^\circ K$ again. As in the first series, the martensite peaks were observed to increase with decreasing temperature in the expected manner while the austenite showed a continuous decrease in $f_T$ with decreasing temperature. In both series of measurements, all peaks returned to their original room temperature intensities when the sample was reheated to 295$^\circ K$.

The measured relative recoilless fractions are compared to the theoretical values in Figure 2. An important aspect of these results is that the $f_T$ value for austenite at 183$^\circ K$ is the same, within precision, for both series of measurements.
IV. Discussion

The reduced value of the recoilless fraction in the austenite at low temperature implies an increase in the probability that a gamma-ray will create a lattice excitation, i.e., that it will be absorbed in a non-recoilless manner. This increasing probability reflects a lessening of lattice resistance to excitation. The energy available from the gamma-ray to create an excitation is, at most, the free atom recoil energy, R. R is determined by the gamma-ray energy and the atomic mass of the atom, and equals $3.1348 \times 10^{-25}$ joules ($1.9567 \times 10^{-3}$ ev) for the Mössbauer transition in $^{57}$Fe [28]. This value is an order of magnitude less than thermal energy at room temperature.

Since at temperatures below $N$ there is a driving energy for the transformation of austenite to martensite which increases with decreasing temperature, such lattice excitations formed in the austenite structure might be related to the martensitic transformation. Without distinguishing between excitations in the form of static distortions or vibrational displacements (such as of soft normal modes) one can conceive of an excitation causing a localized change in the atomic configuration toward the martensitic structure. The behavior of the recoilless fraction of the austenite with decreasing temperature is consistent with such a proposition. The essential independence of the recoilless fraction of the austenite from both the amount of martensite already formed and the immediate tendency to form more martensite indicates that it is at least primarily an intrinsic property of the austenite. This does not necessarily mean that prior treatment (e.g., the formation of the additional amount of martensite at $82^\circ$K) does not change the excitation probability at all, but only that such effects (e.g., as may be due to strains, etc.) are small in comparison to the intrinsic effect.

If the localized excitations are normal vibrational modes enhanced by a lessening of certain elastic constants, a decreasing $f_1$ would imply a decrease in the vibrational characteristic energy required to create the excitation (e.g., the Debye excitation energy given in Equation (2)). If the excitations are different from the normal modes and independent of them, the probability of a recoilless event would take the form:

$$f_T = f_N f_S$$

(4)

where $f_T$ is the measured recoilless fraction at temperature $T$, $f_N$ is the probability that the gamma-ray absorption will not create a normal thermal excitation, and $f_S$ is the probability it will not create a special excitation. If we assume that $f_S = 1$ at 295$^\circ$K and $f_N$ is the Debye value at all temperatures, the temperature variation of $f_S$ and $E^*$ can be estimated (where $E^*$ is the characteristic energy associated with the special excitation and $f_S = \exp(-R/E^*)$). These values are given in Table I. Although the value $E^*$ decreases with temperature the probability of such excitations existing through thermal effects, estimated through the Boltzman factor, $\exp(-E^*/kT)$, does not increase, since the thermal energy, $kT$, decreases more rapidly. If we were to assume that the austenite tendency toward instability onsets well above $N$ the absolute values of the $f_T$'s would be slightly lower. This alternate assumption has only
minor effects on the derived values.

The anomalous decrease in \( f_n \), which amounts to 27% at 82\(^\circ\)K, is too large to be explained in terms of localized instabilities at small metastable regions ("embryos") which are postulated to serve as nucleation centers for martensite. Based on estimates of their size (10^6 atoms) and density (10^2/cm\(^3\)) [29], "embryos" would comprise only 10^-10 of the material. Even if all atoms in an "embryo" behaved as if \( f_n = 0 \), they could not in themselves cause the observed behavior. Thus, the loss of lattice rigidity in the austenite must be a bulk effect, reflecting the overall mechanical instability of this phase at low temperatures.

VI. Summary

The anomalously decreasing recoilless fraction of the austenite with decreasing temperature below ambient is associated with lattice instabilities of this phase, possibly related to its transformation to martensite. The magnitude of the effect indicates that, although the excitations themselves may be localized, they are characteristic of the bulk material and cannot be explained in terms of the conventional theory of pre-existing martensitic embryos. It is unknown whether the gamma-ray induced excitations are stable or unstable. However, in the course of each Mössbauer measurement, it is certain than an appreciable amount of additional martensite has not been formed.

References


**TABLE I: Estimated Values of \( f_s \) and \( E_s^\# \)**

<table>
<thead>
<tr>
<th>T °K</th>
<th>( f_T )</th>
<th>( f_D )</th>
<th>( f_s )</th>
<th>( E_s^# ) (joules)</th>
<th>( \exp(-E_s^#/kT) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>0.778</td>
<td>0.778</td>
<td>1.0</td>
<td>1.95x10^-14</td>
<td>0.0</td>
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<tr>
<td>183</td>
<td>0.720</td>
<td>0.846</td>
<td>0.851</td>
<td>1.01x10^-14</td>
<td>0.463</td>
</tr>
<tr>
<td>82</td>
<td>0.661</td>
<td>0.901</td>
<td>0.734</td>
<td>1.01x10^-14</td>
<td>0.409</td>
</tr>
</tbody>
</table>

FIGURE 1: 295°K Mössbauer Spectrum

FIGURE 2: Temperature Dependence of the Recoilless Fraction; Debye Theory (—) and Experiment.