HIGH TEMPERATURE ELECTRONIC STRUCTURE OF Fe_3O_4 *

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ABSTRACT

The high temperature electronic structure and conduction mechanism in Fe_3O_4 have been investigated through correlations of resistivity and magnetoresistance data with ^{57}Fe NGR. Similar to the resistivity, the relative A and B site isomer shifts are found to decrease rapidly at temperatures well below T_N. Above T_N the A and B site patterns are unexpectedly poorly resolved and this is found to be due to a reduction in the difference in the electronic structure at the two sites. $\delta_B - \delta_A$ is only 0.22 mm s^{-1} at 855 K compared to the expected value of 0.32 mm s^{-1} assuming no change in the relative electronic structures at the two sites on passing through the magnetic order disorder transition. No significant changes in the ^{57}Fe NGR parameters are observed at the conductivity maximum near 400 K. These results require a band model for the conduction mechanism above the Verwey transition and non-negligible conduction electron-ion core interactions for the A site ions above T_N.

INTRODUCTION

Despite the many detailed studies of the Verwey transition in Fe_3O_4, [1,2] controversy still surrounds even a qualitative description of the electronic structure above or below the transition temperature, T_V. The transition has been described variously as a metal-insulator, semiconductor-semiconductor, and semimetal-semiconductor. Much of the recent attention has been devoted to phenomena at or near T_V. However, neither the transition nor the electronic structure of the low temperature phase can be adequately understood in the absence of a valid description of the high temperature phase. In addition, the electrical conductivity of Fe_3O_4 displays some remarkable variations above T_V with a local maximum at ∿400 K and a minimum at ∿50 K below the Néel temperature, T_N.[3] These features of the electrical conductivity are poorly understood and have been subjected only recently to theoretical analysis.[4]

In the present investigation, ^{57}Fe nuclear gamma-ray resonance (NGR) measurements have been made on pure Fe_3O_4 from 77 K to 900 K to determine the change (if any) in the electronic structure giving rise to the conductivity maximum at ∿400 K and the minimum just below T_N. By considering the broad systematics of the data, it was also hoped that a definitive conclusion could be reached concerning the high temperature electronic structure of Fe_3O_4.

Furthermore, because the ^{57}Fe NGR spectrum of Fe_3O_4 above T_N is itself a conundrum, consisting of an apparent single line instead of two, partially resolved lines, a determination of the temperature at which the spectrum deviates from the expected behavior and a rigorous analysis of the line shape above T_N have been made. From earlier measurements[2] it was known that the ^{57}Fe NGR spectrum could be understood up to 750 K in terms of the 300 K spectrum; and consequently, the change in electronic structure giving rise to the apparent, single line above T_N must take place within 100 K of T_N. This result suggests a

possible relationship between the conductivity minimum below T_N and the unusual character of the NGR spectrum above T_N. No ^{57}Fe NGR measurements have been specifically directed at determining possible changes in electronic structure associated with the conductivity maximum at ∿400 K, and this temperature region has also received close attention in the present study.

The results of this study demonstrate that there is indeed a relationship between the unusual character of the ^{57}Fe NGR spectrum above T_N and the conductivity minimum below T_N. The change in electronic structure giving rise to both phenomena appears to be the onset of significant interactions between the A site Fe ions and the conduction electrons and the concomitant increase in spin-disorder scattering. The conductivity maximum at ∿400 K results in no noticeable anomalies in the NGR spectrum and is apparently due to higher order dynamical effects and not to fundamental changes in electronic structure, validating theoretical models.[4,5] The temperature dependence of the NGR parameters from 300 K to 750 K are consistent with band conduction and confirms recent theoretical predictions to this effect.

EXPERIMENTAL

The polycrystalline Fe_3O_4 sample has been described previously, investigated with a number of different techniques and is known to be highly stoichiometric.[2]

The NGR spectrometer consisted of an electro-mechanical velocity drive and a 1024 channel analyzer operated in the so-called "time mode". A 50 mCi Co^{57}/Rh source was employed and maintained at 298 K during the measurements. The spectrometer was calibrated with sodium nitroprusside and iron metal. A commercial design, vacuum furnace was used in the high temperature measurements, and the sample was contained in a boron nitride cup which was in contact with a chromel/alumel thermo-couple. The temperature was controlled with a proportional controller and was stable to within ±2 K of the desired temperature.

RESULTS

The ^{57}Fe NGR spectrum of Fe_3O_4 at 856 K is shown in Fig. 1; T_N for this sample is 855 K. The solid line is the result of a least-mean-squares fit of a single, Lorentzian shaped line to the data. The line in the lower part of Fig. 1, the "residual", is the difference between the fitted line and the experimental data; and the strong structure in the residual demonstrates the inadequacy of the single line fit. Even though the asymetry in the structure of the residual indicates the presence of unresolved structure in the NGR spectrum and not a simple deviation from Lorentzian shape as might result from instrumental and sample preparation effects, attempts to fit more than one line to the spectrum produced physically meaningless results in the absence of doubtful constraints during the fitting procedure.

The spectra below 800 K were straightforward and easily understood on the basis of the 300 K spectrum of Fe_3O_4. They were fitted to two, magnetic hyperfine + electric quadrupole patterns; the magnetic
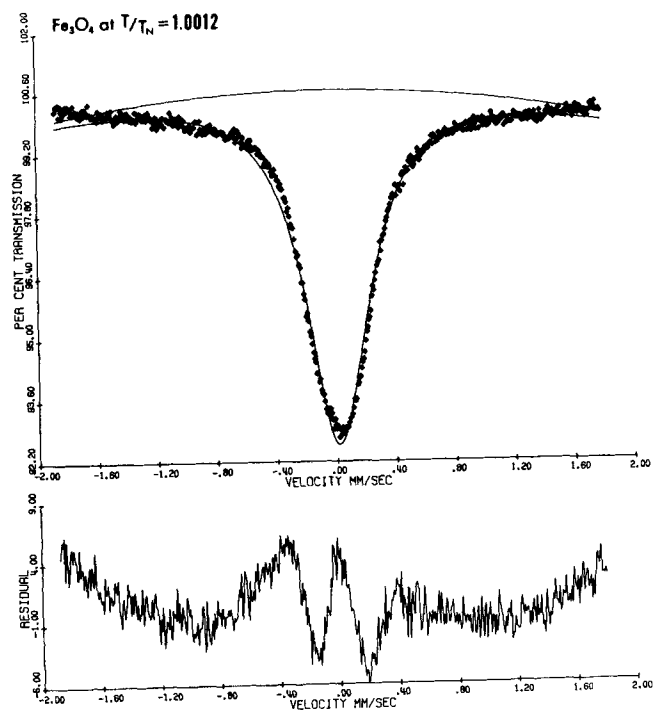
Fig. 1. ^{57}Fe NGR spectrum of Fe$_3$O$_4$ at 856 K (T$_N$ = 855 K). The points are the experimental data and the solid line is the least squares fit of a single, Lorentzian line to the spectrum. The lower line is the difference between the fitted spectrum and the experimental points. The deviations between ∿-0.2 mm s^{-1} and ∿-0.6 mm s^{-1}, at the bottom of the absorption line, and between ∿0.1 mm s^{-1} and ∿0.3 mm s^{-1} are to be noted and compared with Fig. 5. The relative heights of the minima in the residual are also to be compared with those in Fig. 5.

hyperfine field, H(i), isomer shift, δ_i, electric quadrupole interaction, $\Delta E_Q(i)$, line-width, Γ_i, and intensities of each pattern were varied independently until a chi-square, goodness-of-fit criterion was met. The intensities and widths of lines 1, 2, and 3 in a given pattern were constrained to be equal to those lines 4, 5, and 6 of the same pattern.

None of the NGR parameters exhibited unusual behavior in the region of the conductivity maximum near ∿400 K. The difference in hyperfine fields, H(B) - H(A), increased from 30 kG at 300 K to 45 kG at 700 K in qualitative accord with the relative sublattice magnetisations. H(B) - H(A) decreased rapidly above 725 K, but the significance of this decrease is complicated by the rapid fall in magnetisation in this temperature range and will not be considered further. The ratio of the integrated intensity of the B site pattern to the A site pattern decreased from 1.90 at 300 K to 1.70 at 800 K, exhibiting no anomalies and in accord with the recoilless fractions of the two sites. Γ_B/Γ_A is nearly constant from 300 K to 750 K but shows a substantial decrease above this temperature. Surprisingly, the decrease in Γ_B/Γ_A is occasioned primarily by an increase in Γ_A. This increase in the A site line-width is almost certainly related to the isomer shift anomaly to be discussed below.

In contrast to the behavior near 400 K, δ_A exhibited an anomalous increase at 800 K as shown in

Fig. 2; and both δ_A and δ_B decreased rapidly above this temperature. The difference in isomer shifts, $\delta_A - \delta_B$, demonstrates more dramatically this change in isomer shifts as shown in Fig. 3.
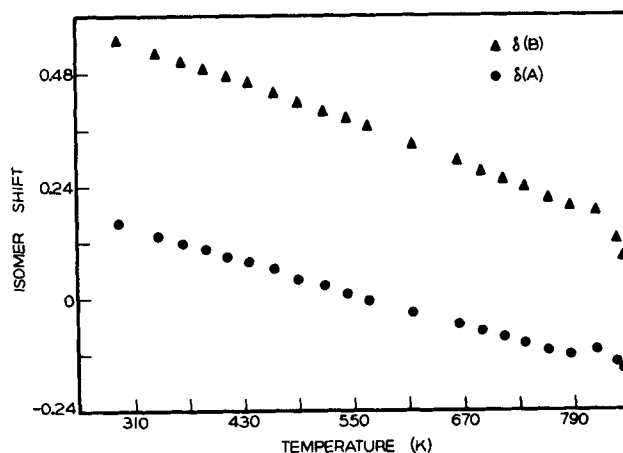

Fig. 2. The temperature dependences of the A and B site isomer shifts, δ(B) and δ(A), respectively. The isomer shifts are relative to a Co^{57}/Rh source at 298 K and are uncorrected for the second-order-Doppler shift. The increase in δ(A) at ∿800 K and the rapid decrease in δ(B) above this temperature are noteworthy. The Néel temperature is offscale on the abscissa.
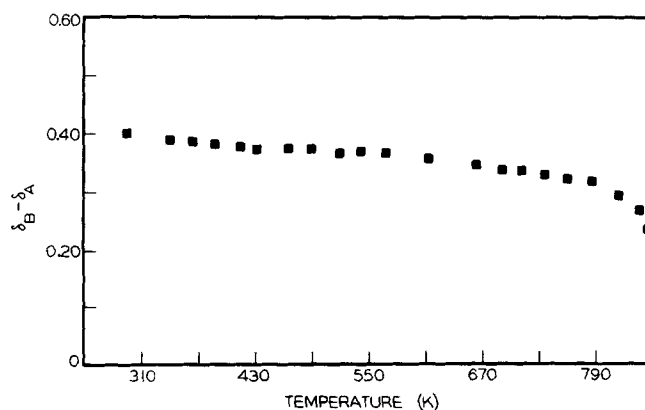

Fig. 3. The temperature dependence of the differential isomer shift at the A and B sites, $\delta_A - \delta_B$. The abrupt decrease above ∿800 K is clearly evident.

DISCUSSION

Insofar as the conductivity maximum near 400 K and the minimum approximately 50 K below T$_N$ are concerned, only δ_i and possibly Γ_i provide insights as to their origins. None of the NGR parameters, including δ_i, shows unusual behavior in the region of the conductivity maximum and it may be safely concluded that the maximum in the conductivity is not caused by a fundamental change or cessation of such change in the

electronic structure. This result provides for the theoretical suggestions that the broad maximum in conductivity is due to dynamical scattering proceese.[4,5]

The temperature dependence of δ_i near the high temperature conductivity minimum indicates that it is to be associated with a change in electronic structure. Below 750 K $d\delta_A/dT$ and $d\delta_B/dT$ have values of -5.84×10^{-4} mm s^{-1} K^{-1} and -7.34×10^{-4} mm s^{-1} K^{-1}, respectively. $\delta_A - \delta_B$ is 0.40 mm s^{-1} at 298 K and on the basis of the above slopes of δ_A and δ_B below 750 K, $\delta_A - \delta_B$ is calculated to be 0.32 mm s^{-1} at 855 K. The NGR spectrum expected on this basis is shown in Fig. 4 and is quite unlike that in Fig. 1. We can now understand the poor resolution of the NGR
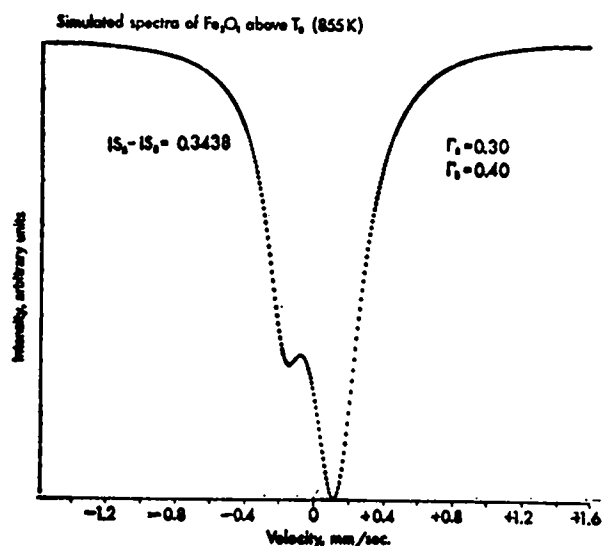

Fig. 4. Computed spectrum of Fe$_3$O$_4$ above the Néel temperature on the assumption that there are no changes in the electronic structure. The more intense line at more positive velocities is due to the B site and the weaker, partially resolved line is due to the A site. The NGR parameters used to compute this spectrum are given in the figure.

spectrum of Fe$_3$O$_4$ above T$_N$ as being a consequence of a change in electronic structure at ~800 K as manifested in the isomer shifts shown in Figs. 2 and 3. The change in electronic structure is such that the s-like electron density at the A site increases relative to that at the B site and approaches that of the B site as T$_N$ is approached.

Even though the spectra above T$_N$ cannot be fitted unambiguously, spectrum simulation permits a semi-quantitative estimate to be made of the isomer shift difference. A large number of spectra were computed in which the B to A site area ratio, Γ_B and Γ_A were assigned values derived from spectra below T$_N$ and $\delta_A - \delta_B$ was varied. These simulated spectra were then "fitted" with the [57]Fe NGR parameters obtained in the fit depicted in Fig. 1. The residual of such a spectrum in Fig. 5 corresponds most closely to the residual in Fig. 1 and indicates an isomer shift difference, $\delta_A - \delta_B$, of 0.22 mm s^{-1}. Thus, the change in electronic structure commencing at ~800 K results in a differential increase of 0.1 mm s^{-1} in
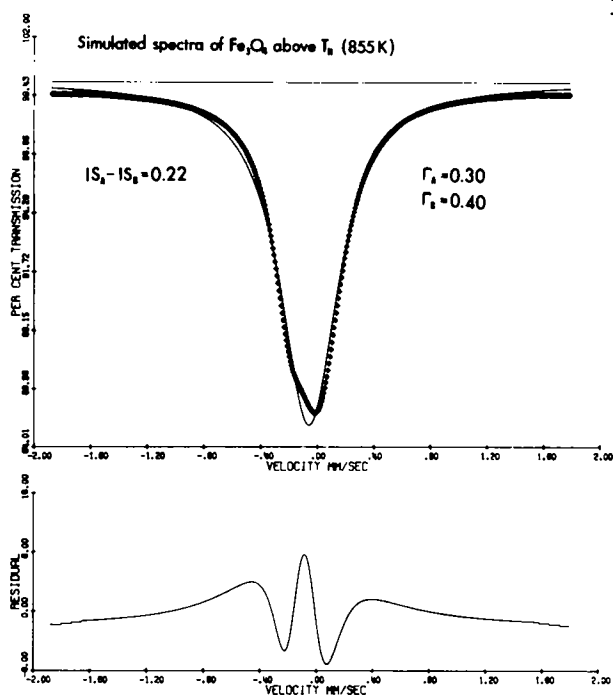

Fig. 5. Simulated spectrum of Fe$_3$O$_4$ above T$_N$. The points are the spectrum calculated assuming an isomer shift difference of 0.22 mm s^{-1} with all other parameters being the same as in Fig. 4. The solid line is the same as the line in Fig. 1. The similarities in the deviations of the line from the points, as indicated in Fig. 1, and the shape of the residual are remarkable.

δ_A relative to δ_B and indicates a significant conduction electron - Fe^{3+}(A) ion core interactions.

An unambiguous mechanism for this interaction is difficult to come by but there are some plausible alternatives. At temperatures as high as 800 K, there is sufficient thermal energy to excite electrons from the B site band into an A site band and the rapid drop in magnetisation lessens the restrictions imposed by the antiparallel A and B site spin directions. It is also probable that a band overlap transition occurs between two, spin-split A and B site bands. Band overlap is permitted by the symmetry of the A and B sublattices. Either of these mechanisms provides an unstrained explanation for the rapid decrease of $\delta_A - \delta_B$ as T$_N$ is approached.

The weak temperature dependence of δ_i and Γ_i below T$_N$ and the absence of any incipient Fe^{2+} character in the NGR spectrum above T$_N$ makes a localized conduction mechanism for Fe$_3$O$_4$ above the Verwey transition unlikely. Thus the high temperature electronic structure of Fe$_3$O$_4$ is best described as that of a narrow-band, metallic or semimetallic, magnetic oxide. The unusual temperature dependence of the conductivity appears to be due to strong electron scattering resulting from temperature dependent magnetisations and electron phonon interactions.

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