Electronic Raman scattering in magnetite: Spin versus charge gap

L. V. Gasparov and A. Rush
Department of Physics, University of North Florida, 1 UNF Drive, Jacksonville, Florida 32224, USA

G. Güntherodt
2 Physikalisches Institut, RWTH-Aachen, 52056 Aachen, Germany

H. Berger
EPFL, CH-1015 Lausanne, Switzerland

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We report Raman-scattering data of single crystals of magnetite (Fe_3O_4) with Verwey transition temperatures (T_v) of 123 and 117 K, respectively. Both single crystals reveal broad electronic background extending up to 900 wave numbers (~110 meV). Redistribution of this background is observed when samples are cooled below T_v. In particular, spectra of the low-temperature phase show diminished background below 300 wave numbers followed by an enhancement of the electronic background between 300 and 400 wave numbers. To enhance the effect of this background redistribution, we divide the spectra just below the transition by the spectra just above the transition. A resultant broad peaklike feature is observed centered at 370 ± 40 wave numbers (45 ± 5 meV). The peak position of this feature does not scale with the transition temperature. We discuss two alternative assignments of this feature to a spin or charge gap in magnetite.

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I. INTRODUCTION

Magnetite (Fe_3O_4) is a naturally occurring mineral which is of interest to remarkably different fields of science. It is the first magnetic material known to mankind and it is the earliest compound known to manifest a charge-ordering transition discovered by Verwey[1] in 1939. Magnetite is also an integral part of many living organisms. For instance, magnetotactic bacteria[2] and pigeons[3] use it for navigation along the Earth's magnetic field. Furthermore, it was reported that magnetite occurs in human brains and may play a role in the pathogenesis of the neurodegenerative diseases such as Alzheimers.[4]

In condensed-matter physics, magnetite has recently attracted substantial attention[5,6] because its charge carriers exhibit strong spin polarization at the Fermi level. This compound has the potential to become one of the leading materials for spintronics. This has initiated an interest in high-quality films of magnetite on a semiconductor substrate. Such films could form the core element of a ferromagnet-semiconductor device.[6]

Magnetite has been extensively studied for more than 60 years, yet the physics of this compound is not completely understood. Competition between electronic, lattice, and magnetic degrees of freedom presents a substantial challenge in describing physics of magnetite. Difficulty in successful modeling of this iron oxide creates a nagging reminder for the scientific community as it tries to tackle such many element compounds as high-temperature superconductors and colossal magnetoresistance compounds.

Verwey transition in magnetite still remains an unsolved puzzle. At ambient pressure, the Verwey transition of pure or near-stoichiometric magnetite is on the first order. This transition occurs at $T_v \sim 123$ K, with changes in crystal structure, latent heat, and a two-order-of-magnitude decrease in dc conductivity. Oxygen deficiency or doping may reduce the transition temperature, may cause the transition to become higher order, or may suppress it completely. There are several competing models of the transition including Verwey and Hayaaman's[7] original order-disorder transition theory, Anderson's[8] long-range order (LRO)-short-range order (SRO) model, Cullen and Callen's[9] theory based on pure electron correlations, and polaron-based theory of the transition.[10–13] However, none of these theories successfully describe the whole body of experimental data. Recently x-ray, neutron-, and electron-diffraction experiments have cast considerable doubt on both Verwey and Hayaaman's order-disorder model and Anderson's LRO-SRO model.[14,15]

Recent photoemission studies[16,17] of magnetite indicate that there is no closing of the electronic band gap at the Verwey transition but rather shrinking of it by about 50 meV. The latter led to the statement that the Verwey transition is not actually metal to insulator transition but rather a semiconductor (or bad metal) to semiconductor transition.[16] In this context, questions naturally arise about the nature and value of the gap in this compound.

Photoemission, with all its advantages, is a surface sensitive technique.[16] Depending on the incoming photon energy, it probes somewhere between 15 and 45 Å. That corresponds to not more than a dozen magnetite unit cells. In contrast, the optical spectroscopy, such as Raman and infrared spectroscopy, probes to the depth of about 1000 Å. Furthermore, the resolution of the optical methods is about one order of magnitude better than that of photoemission. Table I summarizes available data for the gap between the upper edge of single-particle density of states and chemical potential. Note that this gap corresponds to the half of the "optical" gap obtained from the infrared data

The optical band gap detected in the infrared experiment[18,19] may have two origins. It could be the opening of a charge gap but it can also be due to the decrease in carrier mobility because of the polaron "condensation" at the

TABLE I. The value of the gap obtained from the photoemission and optical measurements of magnetite.

Measurement method	Gap above the Verwey transition (meV)	Gap below the Verwey transition (meV)
Photoemission[a]	40	90
Photoemission[b]	100	150
Infrared[c]		70
Infrared[d]		100

[a]Reference 16.
[b]Reference 17.
[c]Reference 18.
[d]Reference 19.

Verwey transition. Unfortunately, it is difficult to separate these two processes.

Raman spectroscopy is a powerful technique capable of addressing the issue of the gap in the magnetite. Such a gap should be manifested in the electronic background of magnetite's Raman spectrum as low intensity broad peaks. One could expect a diminished background at the frequencies smaller than the gap with subsequent increase in the scattering. Similar behavior has been observed in Raman studies of HTSC compounds.[20] Motivated by this fact, we looked for potential signatures of the gap opening in the Raman spectra of Fe_3O_4.

In this paper, we present electronic Raman scattering data obtained on two samples of magnetite grown by two different groups. We believe that we observe a "gap" feature in our spectra. We discuss the origins of this gap, particularly addressing two competing explanations. We conclude that this gap feature we observe has magnetic origin.

II. EXPERIMENTAL DETAILS

In this work, we used two magnetite crystals from two different sources. The first crystal was grown by Berger and co-workers[19,21] in EPFL Lausanne. This was the same crystal used for our previous measurements in magnetite. This crystal was grown by a chemical vapor transport technique using stoichiometric Fe_3O_4 microcrystalline powder obtained by the reduction reaction of ferric oxide (Fe_2O_3). This procedure yielded near-stoichiometric single crystals with typical size of $4\times4\times1$ mm^3. X-ray diffraction confirmed the spinel-like structure of the crystals. Transport measurements detect drop of conductivity at $T_v=123$ K.

The second crystal with $T_V=117$ K was provided by Dr. Pimenov from the University of Wurzburg. This crystal was originally grown by Brabers and crystals from the same batch were used for the photoemission measurements of Ref. 16.

Raman measurements were carried out on freshly cleaved surfaces of the as-grown single crystals. The 532 nm line of a cw solid-state laser as well as 514 and 488 nm lines of an Ar^+ ion laser were used as excitation with no more than 10 mW incident power on the sample, in order to avoid oxidation.[22] Estimated overheating of the sample did not exceed 13 K. Polarized Raman spectra were measured using a Dilor XY modular triple spectrometer equipped with a liquid nitrogen cooled charge-coupled device (CCD) detector. The spectra were measured in nearly back scattering geometry. The sample temperature was maintained in He-bath cryostat over a range of 4.2–300 K.

III. RESULTS AND DISCUSSION

The effects of the Verwey transition on the Raman spectra of magnetite have been addressed in a number of publications.[19,21–27] Below the Verwey transition magnetite has a much bigger unit cell[14] that leads to a dramatic increase in the number of phonon modes. In addition to the phonon modes, magnetite displays a rather broad electronic background extending up to 900 cm^{-1}. Zero-momentum electronic and magnetic excitations in magnetite are likely source of this background.

This paper focuses on the evolution of this background above and below the transition. Figure 1 displays a series of unpolarized spectra of magnetite near the Verwey transition. One can clearly see the enhancement of the low-frequency background in the high-temperature phase. This effect is observed for both samples of magnetite in Figs. 1(a) and 1(b). To understand this enhancement, we need to note that the Stokes Raman-scattering cross section is directly proportional to the imaginary part of the Raman response function χ multiplied by the Bose factor,

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \left\{\frac{1}{1-e^{-\hbar\omega/k_BT}}\right\}\chi''(\omega,T). \quad (1)$$

The imaginary part of the response function contains all the relevant information about quasiparticle excitations in the sample under investigation. The observed background enhancement in the high-temperature phase cannot be accounted by the Bose-factor contribution alone since Eq. (1) would be virtually unchanged over the small temperature shift at the Verwey transition.

To understand the polarization dependence of this enhancement, we measured the polarized spectra of magnetite. Figures 2 and 3 display Raman data in the xx polarization. In both figures, we display the Raman response function obtained by dividing corresponding spectra by the Bose factor. Overheating of 13 K was taken into account. Spectrum below the Verwey transition (solid line) demonstrates redistribution of the electronic background as compared to the spectrum above the transition (dotted line). There is an enhancement of the background above 300 wave numbers and clear depletion of the background below 400 wave numbers.

To underline the redistribution of the background, one can look at the frequency range between 400 and 500 wave numbers. This spectral range has a single phonon mode at 470 cm^{-1} that is absent above the Verwey transition. For this frequency range, both Figs. 2 and 3 indicate that the background below transition is substantially smaller than that above the transition. All this in spite of the fact that additional phonon mode appears in this spectral range below the transition temperature. So even though there is added spec-

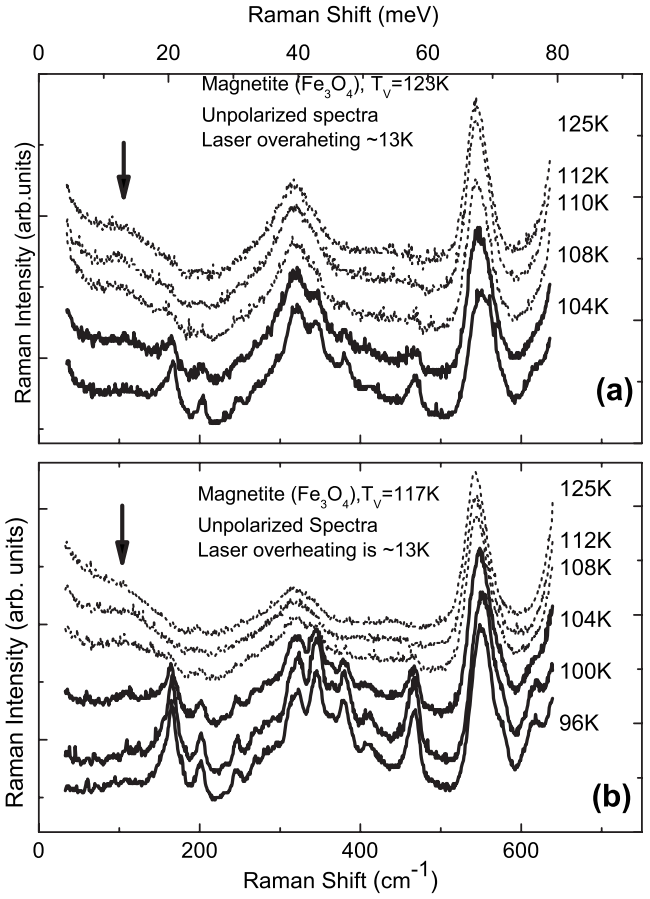

FIG. 1. Unpolarized Raman spectra of magnetite in the XX geometry near Verwey transition in the (a) 123 K and (b) 117 K samples. Spectra are taken with temperature increments of 4 K. Dashed line indicates the spectra above the Verwey transition and solid line indicates the spectra below the Verwey transition. Estimated overheating was around 13 K. Note new phonon modes below the transition and strong redistribution of the electronic background as sample undergoes the transition.

tral weight due to the phonon mode, the background remains diminished compared to the above transition spectrum. We believe that such behavior is consistent with the opening of the gap below 375 wave numbers.

In order to get a better sense of the background redistribution, we divide the response function below the transition temperature by that above the transition. The net result is a peaklike feature with the maximum around 350 wave numbers (insets of Figs. 2 and 3). We assign the peak position of that feature to the value of the gap. Clearly, strong phonon modes in the low-temperature phase do not allow for the precise determination of the gap value; however we believe that the manifestation of the gap opening is evident. Varying the excitation line frequency of our Ar^+ laser did not significantly reduce the phonon mode intensities. Our estimate of the uncertainty of this gap value is 40 wave numbers (~5 meV). This feature is observed only in the XX polarization. Corresponding *XY* spectra did not display any enhancement of the background.

One observes a number of new phonon modes in the low-temperature phase. It is interesting to note that the modes

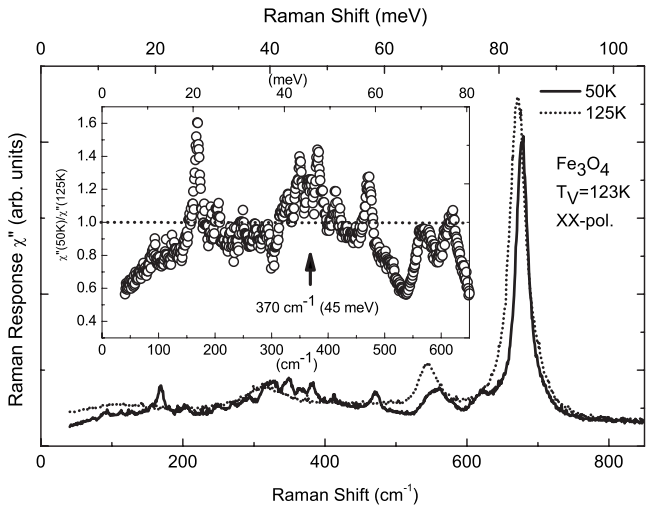

FIG. 2. Polarized (XX geometry) Raman spectra of magnetite with T_v=123 K. Shown are spectra above the transition at 125 K (dashed line) and below the transition at 50 K (solid line). Inset displays the ratio of the 50 K spectrum to that above the transition at 125 K. We assign a broad peaklike feature around 350 wave numbers to the opening of a gap. Horizontal dotted line at the spectra ratio equals to one is a guide for the eyes to appreciate the redistribution of the background.

below 300 cm^{-1} have smaller linewidth compared to the modes above this frequency (Fig. 4). This could be an additional indication of strong interaction of the phonon modes with the opening of the gap

The value of the gap obtained from our experiment is at odds with that from the infrared data. One can make the following suggestions to reconcile these differences. (i) The

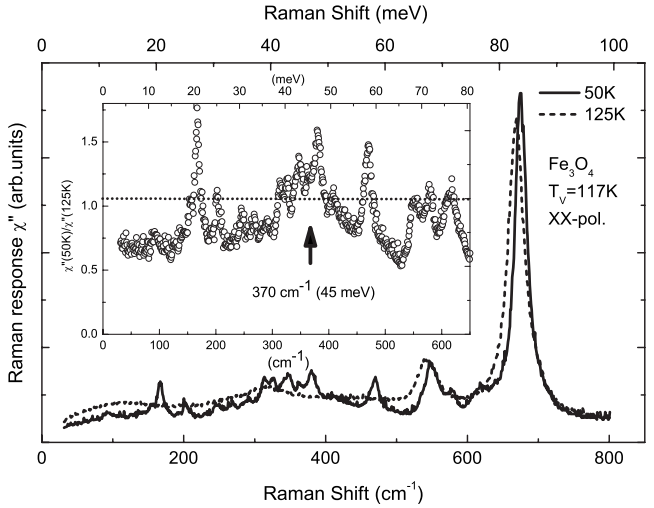

FIG. 3. Polarized (XX geometry) Raman spectra of magnetite with T_v=117 K. Shown are spectra above the transition at 125 K (dashed line) and below the transition at 50 K (solid line). Inset displays the ratio of the 50 K spectrum to that above the transition at 125 K. We assign a broad peaklike feature around 350 wave numbers to the opening of a gap. Horizontal dotted line at the spectra ratio equals to one is a guide for the eyes to appreciate the redistribution of the background.

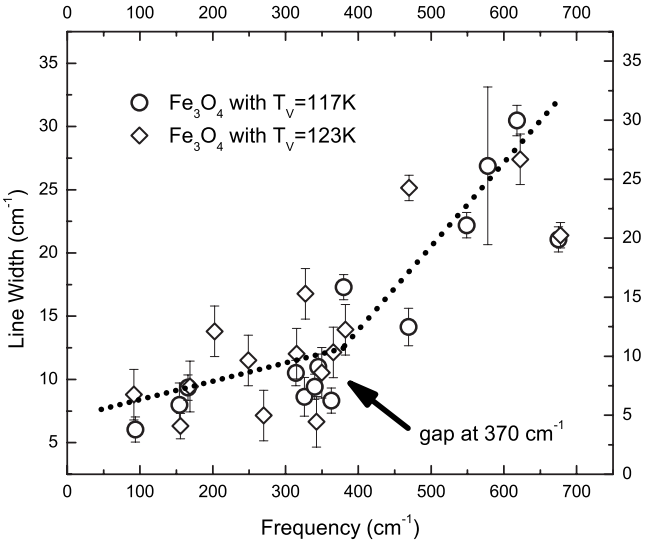

FIG. 4. The linewidth of the phonon modes in the 123 K (open diamonds) and 117 K (open circles) samples as a function of their frequency as measured at 50 K (below the Verwey transition). The linewidth was obtained from the fit to the Lorentzian line shape. Dotted line is a guide for the eyes. Strong increase in the linewidth for the phonon modes above 370 cm^{-1} is evident. The increase is observed in both magnetite samples.

infrared gap[18,19] value may be affected by the increase in carrier mobility associated with the polaron "condensation" at the Verwey transition; (ii) the infrared gap is averaged over whole Brillouin zone (BZ) whereas Raman scattering displays a *k*-dependent charge gap. Photoemission data do indicate strong dependence of the photoemission gap on the crystallographic direction.[16]

Having made these statements, we recognize that differences between the values of the Raman and photoemission/ir gap are nearly a factor of 2 which may be too much to be accounted by the potential anisotropy of the charge gap. Therefore, an alternative explanation of our data is in order.

Such explanation comes from the recent neutron-scattering experiments of McQueeney *et al.*[28] In this work, several acoustic and optical spin-wave modes (magnons) were studied. Some of these magnetic excitations have been originally measured in the seminal neutron-scattering experiment of Brockhouse,[29] however never detected by optical measurements.

McQueeney's neutron data[28] indicated one particular acoustic magnon that is very sensitive to the Verwey transition. Above transition, neutron scattering detects this magnon as a peak at $(4,0,-1/2)$ reciprocal space extending from 30 to 50 meV (roughly 240–500 wave numbers). The magnon peak itself demonstrates isotropic dispersion around the (004) Brillouin-zone center.[28] Below the Verwey transition, this peak splits into two peaks. The latter has been interpreted as an opening of a gap in the acoustic magnon branch. In the reciprocal space, the gap is localized at $\pm 0.1-0.2$ reciprocal-lattice units[28] along (0.0,1) direction. This gap is opening at 43 meV at the wave vector $\mathbf{q}=(0,0,\frac{1}{2})$. This value of the "spin-wave gap" is in excellent agreement with our data.

Raman scattering probes zone-center excitations in solids. Acoustic magnon has zero energy at zero momentum and therefore it cannot be detected through the conventional Raman process. However, two-magnon scattering may alleviate this restriction. The mechanism of this two-magnon scattering assumes the interaction of two magnons with opposite q vectors. Combined excitation will therefore have zero net momentum but nonzero energy. Such excitation is averaged over Brillouin zone and can be probed by the appropriate Raman vertex. Based on this assumption, we would expect two-magnon Raman scattering to manifest itself as a broad peak.[30,31] Furthermore, when the gap develops in the magnon branch we would expect a drop in the intensity of these two-magnon peak beyond the energy of the gap. XX Raman vertex probes over whole BZ. Furthermore, the location of the gap in the magnon branch is consistent with this geometry. Since gap develops at substantially lower temperature, we can also expect narrowing of the two-magnon peak.

In addition to magnetic excitations, one can expect electronic excitations to play important role in the magnetite. In general one should see electronic excitations associated with carriers. The scattering rate[32,33] is related to the slope of the imaginary part of the Raman response function $\frac{\partial \chi''}{\partial \omega}$ in the limit of $\omega \to 0$. The smaller the slope, the shorter is the lifetime τ and the larger is the scattering rate $\Gamma = 1/\tau$. Resistivity is directly proportional to the scattering rate. When magnetite undergoes the Verwey transition, its resistivity increases by about two orders of magnitude. The latter means that the carrier scattering rate should exhibit a jump at the transition. That means that the low-temperature spectrum of magnetite should display low-frequency scattering characterized by substantially flatter slope. That is indeed the case in our experiment.

This "spin gap" may be associated with the optical phonon mode crossing the acoustic magnon branch. McQueeney *et al.*[28] indicated possible flattening of the magnon branch at the opening of the gap. Such flattening may create a peaklike singularity in Raman data, as we observe in our data.

Additional evidence for the spin gap nature of the observed Raman effects may come from the phonon linewidths displayed in Fig. 4. Below the transition in both samples, the phonon modes become substantially broader above 370–380 cm^{-1}. This is likely an indication of strong coupling between magnetic and lattice excitations (hence, XX polarization of the "spin gap" effects[34]), providing additional evidence of the spin gap. One should keep in mind that most of these modes are associated with the same Fe-O tetrahedron; therefore the increase may not be interpreted as merely different groups of ions that are somehow more affected by the disorder. Increase in the linewidth is likely an indicator of additional decay channel for the phonons.

The XX geometry above the transition displays just three phonon modes (Figs. 1 and 2). These modes are centered at 310, 545, and 670 cm^{-1} (Figs. 1 and 2). The widths of the modes at 150 K are 60, 29, and 63 wave numbers, respectively. Clearly these numbers do not follow the low-temperature trend displayed in Fig. 4. Only below the transition we observe a broadening of the modes centered above 370 wave numbers. This clearly dovetails the idea of the spin gap opening effect on the phonon modes width. It is there-

fore plausible to assign the 45 meV feature we observed in the Raman spectrum to the "spin-wave gap." This assignment, however reasonable, assumes that the charge gap is absent in Raman. This is probably due to small matrix elements for these particular excitations. We are not aware of any theoretical work addressing the issue of Raman tensors and the charge gap in magnetite. Our result points out the need for such calculations. Further experiments with Fe ions substituted by nonmagnetic ions will shed more light on to this issue.

IV. CONCLUSION

In conclusion, we present the Raman measurements of the electronic background in magnetite. Comparison of the spectra above and below the Verwey transition yields the gap value of the order of 45 ± 5 meV, which is in excellent agreement with recent neutron-scattering data on the spin-wave gap at 43 meV.

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