Far-infrared optical properties of antiferromagnetic $SmTiO_3$

M. G. Hildebrand, A. Slepkov, and M. Reedyk
Department of Physics, Brock University, St. Catharines, Ontario, Canada L2S 3A1

G. Amow and J. E. Greedan
Department of Chemistry and Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L2S 4M1

D. A. Crandles
Department of Physics, Franklin and Marshall College, Lancaster, Pennsylvania 17604
(Received 3 December 1997; revised manuscript received 28 September 1998)

The polarized reflectance of nominally stoichiometric $SmTiO_3$ has been measured in the far-infrared at temperatures above and below the antiferromagnetic Néel temperature T_N of 50 K. The appearance of a feature near 120 cm^{-1} when the electric field vector is polarized along the *b* axis correlates with the onset of magnetic ordering in the Ti and Sm sublattices, suggesting it is likely due to a magnetic transition. Its large linewidth and relatively high-energy scale point to a two-magnon process. Because the $RTiO_3$ family of compounds (where *R* is a rare earth or Y) is susceptible to doping by vacancies on the *R* site, the nominally stoichiometric sample examined has a small, but finite background conductivity of the order 20 $\Omega^{-1}cm^{-1}$ at low frequencies. This background conductivity, like that along the semiconducting *c* axis in underdoped cuprate superconductors, appears to be of an incoherent nature with a magnitude below Mott's minimum metallic conductivity. At temperatures below T_N there is evidence that the continuum interacts strongly with a nearby allowed phonon mode causing considerable asymmetry. The correlation between the onset of magnetic ordering and the appearance of asymmetry in the allowed phonon mode suggests that this continuum, to which the mode appears to be strongly coupled, may be of magnetic origin. [S0163-1829(99)09209-7]

I. INTRODUCTION

The $RTiO_3$ family of compounds (where *R* is a rare earth or Y) has experienced increased interest recently. Like the cuprate-based high-T_c superconductors these compounds can be doped using a variety of mechanisms (excess oxygen, chemical substitution, cation vacancies) to yield materials ranging from highly correlated magnetic insulators to poor metals. The electronic and magnetic temperature-doping phase diagram of the titanites has been discussed by Tokura.[1] Considerable effort has been put forth to study the progression of the optical properties with doping using varied spectroscopic techniques including photoemission,[2] reflectance,[3] and Raman scattering.[4] Unlike the cuprate superconductors which are derived from an antiferromagnetic parent compound which is a charge-transfer insulator with the gap formed between occupied oxygen $2p$ states and the unoccupied copper $3d$ states of the upper Hubbard band, insulating $RTiO_3$ is a Mott insulator with the gap formed between correlated Ti $3d$ states of the lower and upper Hubbard band. Here we focus our attention on the nominally stoichiometric member $SmTiO_3$, and investigate the far-infrared optical properties at low temperatures where the Ti and Sm sublattices are in a state of antiferromagnetic order.

Far-infrared spectroscopy has proven to be a valuable tool for the investigation of materials with magnetic phase transitions. Paramagnetic, ferromagnetic, and antiferromagnetic insulators were studied extensively for magnetic resonances in the 1960's.[5] Magnetic phenomena were also found to influence the optical properties of certain metallic materials. For example, the optical properties of chromium were observed to be affected by an antiferromagnetic energy gap.[6] Such spin-density-wave gaps have since been found in more exotic metals such as the heavy fermion compounds URu_2Si_2 (Refs. 7,8) and UCu_5.[8] Recently it has been established that the cuprate superconductors have a pseudogap in the *c*-axis optical conductivity which is believed to be due to the opening of a gap in the spectrum of spin excitations which affects the conductivity (charge transport) via an interaction between the charge and spin excitations.[9] Furthermore, the in-plane midinfrared spectrum of undoped and very lightly doped cuprates is characterized by a weak absorption, generally thought to be magnetic in origin.[10] Since the mechanism underlying the high-temperature superconductivity is not yet fully understood, but is widely believed to arise from magnetic interactions, it is of considerable interest to investigate the effect of magnetic ordering on the optical properties of other perovskite-based oxides.

II. EXPERIMENTAL

Single crystals of nominally stoichiometric $SmTiO_3$ were synthesized[11] by heating a previously prepared polycrystalline sample of this material to just above its melting point of 1800 °C and quenching to room temperature. To avoid oxidation the product of the reaction was carried out under a vacuum of 10^{-6} Torr in an induction furnace. A crystal was selected and its orientation was determined using the Laue x-ray-diffraction technique. Magnetization was measured using a Quantum Design superconducting quantum interference device dc magnetometer. The far-infrared reflectance measurements were carried out at temperatures ranging from 0.6 to 90 K using a Martin-Puplett-type polarizing interferometer and a Helium-3 Cryostat. This interferometer is optimized for the very far infrared, and allowed reliable data to be obtained to frequencies as low as 5 cm^{-1}. The midinfra-

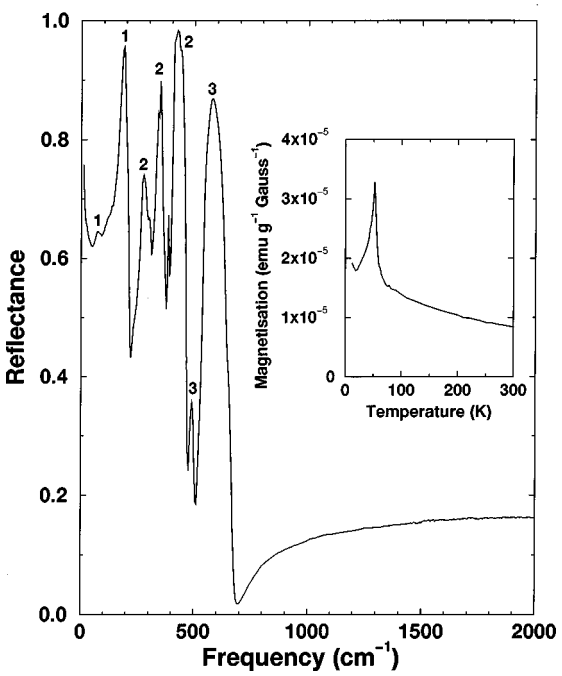

FIG. 1. The unpolarized reflectance of nominally stoichiometric $SmTiO_3$ at 60 K (main figure). Modes labeled 1, 2, and 3 are assigned to the three main vibrational bands associated with the cubic ABO_3 perovskite structure: the external mode (TiO_6 octahedron vibrates against the rare-earth atoms), and the internal Ti-O bending and stretching modes, respectively. Note the upturn in the reflectance towards unity at the lowest frequencies. The inset gives the magnetization of the same crystal showing clearly the antiferromagnetic transition near 50 K.

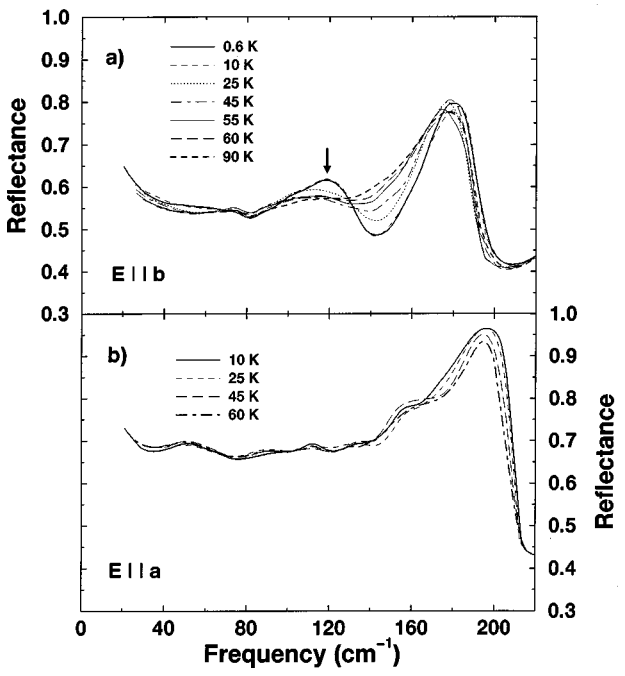

FIG. 2. Low-frequency reflectance of $SmTiO_3$ with the electric-field vector **E** polarized along (a) the *b* axis and (b) the *a* axis at several temperatures. Note the appearance of a feature in the *b*-axis spectrum near 120 cm^{-1} (indicated by an arrow) at temperatures below the antiferromagnetic Néel temperature.

red reflectance was measured at liquid-nitrogen temperature using a Bomem Michelson Interferometer for frequencies up to 5000 cm^{-1}. In both cases an *in situ* gold evaporation was used to obtain the absolute reflectance.[12] High-frequency extensions to enable Kramers-Kronig analysis to obtain the optical conductivity were taken from previous room-temperature data.[13]

III. RESULTS AND DISCUSSION

Figure 1 shows a portion of the composite unpolarized spectrum obtained for far-infrared measurements carried out at 60 K. As discussed previously for room-temperature spectra of the $RTiO_3$ series,[14] the phonon spectrum consists of the three main vibrational bands associated with the cubic ABO_3 perovskite structure, which are split into several resolvable modes (in particular the central band) due to an orthorhombic distortion. The central band, and the highest frequency band, comprised of the components labeled 2 and 3, respectively, have been assigned to the internal Ti-O bending and stretching motions of the TiO_6 octahedron, respectively. The lowest frequency band which appears to consist of the two resolvable components labeled 1 in the figure is assigned to the external mode in which the TiO_6 octahedron vibrates against the rare-earth atoms. The just-barely resolved component near 70 cm^{-1} was not identified in the previous room-temperature work[14] because the measurements did not extend as low in frequency. A mode with similar frequency and oscillator strength does however appear in spectra of the isostructural rare-earth orthoferrite $LaFeO_3$ (Ref. 15) and, therefore, we identify it as an ordinary allowed phonon mode.

The distorted orthorhombic perovskite crystal structure of $SmTiO_3$ belongs to the *Pnma* space group.[11] The lattice constants of the crystal used in the optical investigation were found to be $a=5.635$ Å, $b=7.725$ Å, and $c=5.440$ Å. A full group-theoretical analysis of the expected infrared-active phonon modes in this coordinate system yields $9B_{1u}+7B_{2u}+9B_{3u}$.[16] Polarized reflectance measurements were carried out in the far-infrared along all three axes. The results for the long axis *b* and one of the two short axes *a* are shown in Fig. 2.

As is clear from the magnetization, shown in the inset of Fig. 1, upon lowering the temperature to 50 K the sample undergoes a transition to an antiferromagnetic state. More extensive magnetic and neutron-diffraction measurements on $Sm_{1-x}TiO_3$ samples further support this conclusion and show that antiferromagnetic order is well established for small *x*, disappearing at $x=0.10$.[11] Similar observations have been made for the $Nd_{1-x}TiO_3$ system.[17] The low-temperature single-crystal neutron-diffraction measurements of a $Sm_{0.97}TiO_3$ crystal from the same growth batch as that investigated optically estimated the magnetic moments to be $0.72(1)\mu_B$ and $0.43(1)\mu_B$ on the Ti and Sm sublattices, respectively. The Ti spins were found to be oriented primarily along the *a* axis with a $7\pm3°$ tilt towards the *b* axis, while the Sm spins were oriented at $2\pm2°$ to the *c* axis. A small ferromagneticlike component to the magnetization, of unknown origin, also exists.

While the similar *a*- and *c*-axis spectra showed a moderate temperature dependence of the phonon band as can be seen for the *a* axis in Fig. 2(b), the onset of antiferromag-

netism was accompanied by an interesting change in the *b*-axis spectrum. As shown in Fig. 2(a), a strongly temperature-dependent feature emerges out of the low-frequency shoulder of the phonon situated near 180 cm^{-1}. Since x-ray and neutron-diffraction measurements[11] at temperatures as low as 1.5 K show no evidence of a structural phase transition, and the emergence of this feature coincides with the onset of magnetic ordering we assign it to a magnetic resonance. Note that on a much smaller scale, the *a*-axis spectrum of Fig. 2(b) shows some similarities.

Antiferromagnetic resonance (AFMR) modes were observed experimentally using the technique of far-infrared transmission spectroscopy by Kondoh on NiO in 1960,[18] and Ohlmann and Tinkham in 1961 on FeF_2,[19] after their existence was predicted theoretically by Kittel in 1951.[20] AFMR modes have since been observed in transmission in a number of compounds. In 1982, Häussler *et al.* investigating FeF_2 and CoF_2 observed these magnetic resonances by means of reflectance spectroscopy.[21] AFMR modes correspond to zone-center ($\mathbf{k}\approx 0$) excitations and usually occur at very low frequencies in the far infrared. Following the experimental confirmation of AFMR modes, it was discovered that additional absorption, resulting from the excitation of two magnons with equal and opposite **k** vector, may be observed at higher energy.[22] Because the magnon density of states is typically peaked at points on the Brillouin-zone boundary the two-magnon absorption can appear at frequencies considerably higher than twice the energy of the zone-center AFMR mode. In MnF_2, for example, which has a Néel temperature of 67.7 K, the AFMR mode is found at 8.7 cm^{-1} while the two-magnon absorption occurs near 100 cm^{-1}.[23] The two-magnon absorption can be of equal, or even greater intensity than that of the AFMR. These two types of modes can be further distinguished by the linewidth of the absorption feature. Because the two-magnon mode is influenced by the **k**-dependent magnon density of states it is typically much broader than the AFMR mode.

In Fig. 3 (main) we present the Kramers-Krönig derived optical conductivity for *b*-axis polarized $SmTiO_3$ at several temperatures. Each successive curve has been shifted by 100 $\Omega^{-1}cm^{-1}$ for clarity. The feature we identify as a magnetic excitation (M) is indicated. Given that for the relatively low Néel temperature of 50 K, the mode has a high energy scale (120 cm^{-1}) and considerable linewidth, we assign it to a two-magnon process. Further support for this conclusion can be drawn from a comparison with light-scattering experiments on magnons in other perovskite-based antiferromagnets. For example, $KNiF_3$, $RbMnF_3$, and $RbCoF_3$ have the simple cubic perovskite structure with antiferromagnetic Néel temperatures of 245, 101, and 82.5 K, respectively. Two-magnon modes are found at 750, 336, and 133 cm^{-1}, respectively, while single-magnon modes have been observed for $KNiF_3$ and $RbCoF_3$ at 4.5 and 31 cm^{-1}, respectively.[24] Note that to within factors of two, the two-magnon energy scales roughly with T_N. The rare-earth orthoferrites, $RFeO_3$, which have a slightly distorted perovskite structure and are isostructural to $RTiO_3$, have Néel temperatures ranging from 640 to 690 K depending on *R*. One-magnon scattering is found in the region from 10–20 cm^{-1}, while two-magnon scattering occurs on a much higher energy scale of 1000 cm^{-1}.[25] To a first approximation, an order of magnitude scaling based on the ratio of the Néel temperatures suggests magnetic excitations on the order of 100 cm^{-1} in $SmTiO_3$ would be associated with a two-magnon process, while AFMR modes might only be expected below the spectral range investigated.

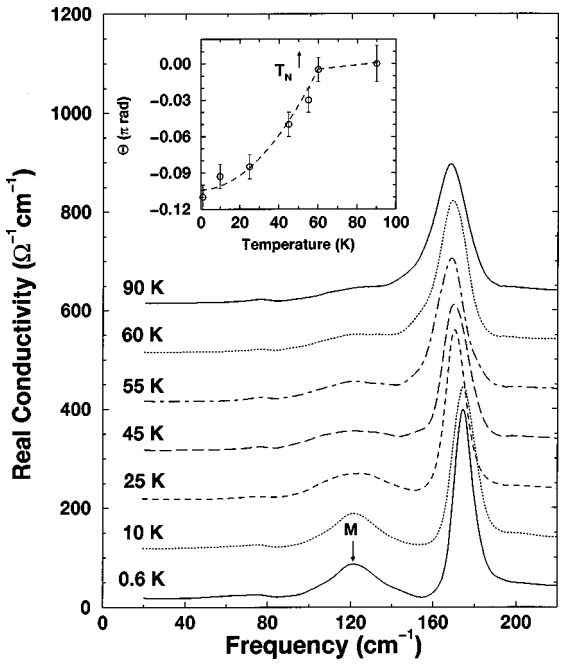

FIG. 3. Kramers-Kronig derived low-frequency optical conductivity of *b*-axis polarized $SmTiO_3$ at several temperatures (main figure). Successive curves have been shifted by 100 $\Omega^{-1}cm^{-1}$ for clarity. Note the growth of the feature near 120 cm^{-1} (labeled M) at temperatures below the antiferromagnetic ordering temperature of 50 K. Note also the small but finite background conductivity. The inset shows the temperature dependence of the parameter θ which characterizes the asymmetry of the phonon mode as defined in the text. Dashed lines are a guide to the eye. Note the increase in asymmetry below the magnetic ordering temperature T_N.

The low-frequency shoulder in the reflectance of the phonon band at higher temperatures gives rise to a step in the optical conductivity near 100 cm^{-1} of approximately 20 $\Omega^{-1}cm^{-1}$. This increased level of background conductivity continues on the high-frequency side of the mode which has a symmetric Lorenzian-like form. It is not clear whether at lower temperatures the magnetic peak develops out of this shoulder or is a new entity. However, even if the mode were present above T_N, this would not strictly preclude a magnetic origin. Two-magnon modes have been observed in light-scattering experiments to temperatures as high as $4T_N$.[24] Further support for a magnetic origin to this mode can be taken from the fact that it is observed only along the *b* axis where the group-theoretical analysis bears out the least number of expected phonon modes. It is therefore highly unlikely that this is simply a weak mode which becomes resolved at low temperatures. It is interesting that this feature appears in the *b*-axis spectrum while the Ti and Sm spins sit primarily in the *ac* plane suggesting that it is the canting of the spins towards the *b* axis, or the small ferromagnetic component, that plays an important role.

The temperature dependence of the 175 cm^{-1} phonon mode is also noteworthy. At low temperature it begins to

take on a form highly reminiscent of the Fano-like resonance which results when a single narrow mode interacts with a broad background.[26] This might be regarded as surprising given the fact that the sample is nominally stoichiometric and insulating. The $R\mathrm{TiO}_3$ family of compounds is however, as alluded to above, susceptible to doping by vacancies on the R site.[27] In fact, the Sm-site occupancy was determined from a structural refinement of single-crystal x-ray data obtained using a crystal from the same batch as the sample studied here, yielding a composition of $\mathrm{Sm}_{0.97}\mathrm{TiO}_3$.[11] These observations are also in keeping with recent Raman-scattering measurements on the nominally stoichiometric $R\mathrm{TiO}_3$ series which found evidence for an electronic scattering background, to which certain phonons were coupled strongly as indicated by such a Fano-like asymmetry.[16] Moreover, the reflectance of Fig. 2 which is seen to rise towards unity at low frequencies also suggests the presence of a small background continuum, which from the optical conductivity of Fig. 3, derived assuming this to be the case, is of the order 20 $\Omega^{-1}\mathrm{cm}^{-1}$ along the b axis.

The presence of this continuum, attributed to doping by vacancies on the rare-earth site, and corroborated by the Raman work, is interesting given that the electrons are believed to exist in localized states in these magnetic insulators. The fact that the magnitude is significantly lower than Mott's minimum metallic conductivity limit[28] and that the dc resistivity exhibits a semiconductinglike negative temperature coefficient[11] suggests incoherent transport. This decidedly non-Drude-like behavior, and the absolute level of the background optical conductivity is typical[9,29] of that along the semiconducting c axis of many of the underdoped cuprate superconductors which are built of similar perovskitelike layers, suggesting there could be a common origin to this unusual transport.

Some insight into the origin of this background conductivity may be gleaned by considering the temperature dependence of the 175 cm^{-1} phonon mode. One finds that it appears to be strongly influenced in the vicinity of the antiferromagnetic phase transition. Because there are some difficulties encountered in a direct application of the Fano formalism to describe the real optical conductivity,[30] σ_1 it was fitted to the form:

$$\sigma_1 = C + A\omega + \frac{\omega}{4\pi}\,\mathrm{Im} \times\left[\frac{\omega_{PM}^2}{\omega_M^2-\omega^2-i\omega\Gamma_M}+\frac{\omega_{P\mathrm{ph}}^2}{\omega_{\mathrm{ph}}^2-\omega^2-i\omega\Gamma_{\mathrm{ph}}}e^{i\theta}\right]. \quad (1)$$

The linear term is used to represent the nonzero background conductivity, while the two oscillator terms represent the magnetic excitation and the phonon mode which are characterized by the positions of their center frequencies, ω_M and ω_{ph} respectively, their linewidths, Γ_M and Γ_{ph}, and their oscillator strengths, ω_{PM}, and $\omega_{P\mathrm{ph}}$. The multiplicative factor of $e^{i\theta}$ allows for an asymmetric line shape to the phonon. It was found that the position of the magnetic excitation remained essentially constant as the temperature decreased while its oscillator strength increased dramatically and its linewidth decreased. The phonon mode was found to harden and narrow with decreasing temperature and to exhibit a small decrease in oscillator strength, possibly suggesting some transfer to the magnetic resonance. Of greatest interest is the behavior of the parameter θ which characterizes the asymmetry of the phonon mode. Its temperature dependence is shown in the inset to Fig. 3. Note that above T_N that θ is essentially zero, indicating that the mode can be described by a symmetric Lorentzian while the onset of magnetic ordering at lower temperature causes the mode to become increasingly more asymmetric. Since this mode appears to be coupled to the continuum, as evidenced by the pronounced asymmetry, and furthermore is noticeably affected by the magnetic phase transition, one might speculate that the background conductivity is of magnetic origin, or at least, as is believed to be the case for the c-axis conductivity of the cuprates, strongly influenced by an interaction between charge and spin excitations.

IV. CONCLUSIONS

In conclusion, in addition to the expected phonon spectrum consisting of three main vibrational bands, measurements of the low-temperature far-infrared reflectance of nominally stoichiometric SmTiO_3 have revealed two further characteristic features of the optical properties; the presence of a mode near 120 cm^{-1} with the electric field vector polarized along the b axis at temperatures below the onset of antiferromagnetic order in the Ti and Sm sublattices, and a non-Drude background with a magnitude below Mott's limiting minimum metallic conductivity. In addition, the lowest frequency allowed phonon band, corresponding to vibrations of the rare-earth atoms against the TiO_6 cage, takes on a very asymmetric appearance below T_N, indicative of a strong interaction with this continuum which may be of magnetic origin. The mode is interpreted to be due to a two-magnon process.

ACKNOWLEDGMENTS

We thank F.S. Razavi for the use of the magnetometer, and J. Britten for determining the lattice constants of the crystal investigated. We are grateful to T. Timusk for helpful comments. Financial support was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

[1] Y. Tokura, J. Phys. Chem. Solids **53**, 1619 (1992).

[2] A. Fujimori, J. Phys. Chem. Solids **53**, 1595 (1992).

[3] Y. Fujishima, Y. Tokura, T. Arima, and S. Uchida, Phys. Rev. B **46**, 11 167 (1992); Y. Taguchi, Y. Tokura, T. Arima, and F. Inaba, *ibid.* **48**, 511 (1993); D.A. Crandles, T. Timusk, J.D. Garrett, and J.E. Greedan, *ibid.* **49**, 16 207 (1994); T. Katsufuji Y. Okimoto, and Y. Tokura, Phys. Rev. Lett. **75**, 3497 (1995).

[4] T. Katsufuji and Y. Tokura, Phys. Rev. B **49**, 4372 (1994).

[5] For a review, see, I.F. Silvera, in *Far-Infrared Spectroscopy*, edited by K.D. Möller and W.G. Rothschild (Wiley-Interscience,

New York, 1970); L.C. Robinson, *Methods of Experimental Physics*, edited by L. Marton and C. Marton (Academic, New York, 1973), Vol. 10.

[6] A.S. Barker, Jr., B.I. Halperin, and T.M. Rice, Phys. Rev. Lett. **20**, 384 (1968).

[7] D.A. Bonn, J.D. Garrett, and T. Timusk, Phys. Rev. Lett. **61**, 1305 (1988).

[8] L. Degiorgi, St. Thieme, H.R. Ott, M. Dressel, G. Gruner, Y. Dalichaouch, M.B. Maple, Z. Fisk, C. Geibel, and F. Steglich, Z. Phys. B **102**, 367 (1997).

[9] C.C. Homes, T. Timusk, R. Liang, D.A. Bonn, and W.N. Hardy, Phys. Rev. Lett. **71**, 1645 (1993); Physica C **254**, 265 (1995).

[10] J.D. Perkins, J.M. Graybeal, M.A. Kastner, R.J. Birgeneau, J.P. Falck, and M. Greven, Phys. Rev. Lett. **71**, 1621 (1993); M. Gruninger, J. Munzel, A. Gaymann, A. Zibold, H.P. Geserich, and T. Kopp, Europhys. Lett. **35**, 55 (1996); A. Zibold, H.L. Liu, D.B. Tanner, J.Y. Wang, M. Gruninger, H.P. Geserich, T. Kopp, Th. Wolf, W. Widder, and H.F. Braun, Phys. Rev. B **55**, 11 096 (1997).

[11] G. Amow, J.E. Greedan, and C. Ritter, J. Solid State Chem. **141**, 262 (1998).

[12] C.C. Homes, M. Reedyk, D.A. Crandles, and T. Timusk, Appl. Opt. **32**, 2976 (1993).

[13] D.A. Crandles, T. Timusk, J.D. Garrett, and J.E. Greedan, Physica C **201**, 407 (1992).

[14] D.A. Crandles, T. Timusk, J.D. Garrett, and J.E. Greedan, Phys. Rev. B **49**, 4299 (1994).

[15] S. Tajima, A. Masaki, S. Uchida, T. Matsuura, K. Fueki, and S. Sugai, J. Phys. C **20**, 3469 (1987).

[16] M. Reedyk, D.A. Crandles, M. Cardona, J.D. Garrett, and J.E. Greedan, Phys. Rev. B **55**, 1442 (1997). Note that in this work the crystal axes are given in *Pbnm* notation, while the group-theoretical analysis was carried out for the *Pnma* coordinate axis orientation.

[17] G. Amow and J.E. Greedan, J. Solid State Chem. **121**, 443 (1996).

[18] H. Kondoh, J. Phys. Soc. Jpn. **15**, 1970 (1960).

[19] R.C. Ohlmann and M. Tinkham, Phys. Rev. **123**, 425 (1961).

[20] C. Kittel, Phys. Rev. **82**, 565 (1951).

[21] K.M. Häussler, A. Lehmeyer, and L. Merten, Phys. Status Solidi B **111**, 513 (1982).

[22] J.W. Halley and I.F. Silvera, Phys. Rev. Lett. **15**, 654 (1965).

[23] S.J. Allen, Jr., R. Loudon, and P.L. Richards, Phys. Rev. Lett. **16**, 463 (1966).

[24] M.G. Cottam and D.J. Lockwood, *Light Scattering in Magnetic Solids* (Wiley, New York, 1986), and references therein.

[25] N. Koshizuka and K. Hayashi, J. Phys. Soc. Jpn. **57**, 4418 (1988).

[26] U. Fano, Phys. Rev. **124**, 1866 (1961).

[27] M.J. MacEachern, H. Dabkowska, J.D. Garrett, G. Amow, W. Gong, G. Liu, and J.E. Greedan, Chem. Mater. **6**, 2092 (1994).

[28] Sir N. Mott, *Conduction in Non-Crystalline Materials* (Clarendon, Oxford, 1987), p. 26.

[29] D.N. Basov, T. Timusk, B. Dabrowski, and J.D. Jorgensen, Phys. Rev. B **50**, 3511 (1994); D.N. Basov, H.A. Mook, B. Dabrowski, and T. Timusk, *ibid.* **52**, R13 141 (1995); S. Uchida, K. Tamasaku, and S. Tajima, *ibid.* **53**, 14 558 (1996); M. Reedyk, T. Timusk, Y.-W. Hsueh, B.W. Statt, J.S. Xue, and J.E. Greedan, *ibid.* **56**, 9129 (1997).

[30] See, for example, the discussion in Ref. 9.