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2004 J. Phys.: Condens. Matter 16 8311

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# Temperature and composition dependence of phonon modes in $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$

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Received 30 June 2004, in final form 20 October 2004

Published 5 November 2004

Online at [stacks.iop.org/JPhysCM/16/8311](http://stacks.iop.org/JPhysCM/16/8311)

doi:10.1088/0953-8984/16/46/017

## Abstract

Low temperature infrared absorption measurements have been carried out on  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$  between 300 and 10 K. With the lowering of temperature, below the magnetic transition temperature,  $T_M$ , the modes corresponding to vibrations of ruthenium and planar oxygen atoms are observed to harden significantly, over and above that determined by anharmonicity, and this is attributed to the spin-phonon interaction. The mode corresponding to the vibrations of the apical oxygen has an asymmetric (Fano) lineshape, and the asymmetry parameter is seen to decrease sharply below  $T_M$ , and a similar behaviour is also seen for Cu-doped  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$  ( $x = 0.0$ – $0.20$ ). This has been understood in terms of the coupling of this phonon mode with the charge carriers. A plot of the phonon linewidth with the square of the Fano asymmetry parameter shows a linear correlation, with a slope dependent on the density of carriers. This slope and the mode frequencies of the various Cu doped samples are seen to correlate with the observed non-monotonic variation of  $T_c$  with Cu content with a maximum for  $x = 0.1$ .

## 1. Introduction

The rutheno-cuprate  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$  (Gd1212, for short), which has a structure similar to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , is an interesting compound that exhibits the remarkable property of the coexistence of superconductivity and magnetism [1], the former arising from the  $\text{CuO}_2$  planes and the latter from the Ru sublattice. It has a  $T_c$  onset of  $\sim 45$  K and a  $T_M$ , the magnetic ordering temperature, of  $\sim 132$  K. At first, the nature of magnetic order in this compound was thought to be ferromagnetic [1, 2]. This raised the interesting question of how superconductivity and ferromagnetism could coexist at the microscopic level [3]. But subsequent neutron

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diffraction experiments [4] as well as band structure calculations [5] based on LDA indicate a predominantly antiferromagnetic (AFM) phase below  $T_M$ . A recent report by Ovchinnikov [6] based on a three-band model of the electronic structure also favours the stabilization of the AFM state in  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$ . The structural changes occurring in this compound at low temperatures have been followed by neutron diffraction [7] as well as x-ray diffraction [8] measurements. The temperature dependences of vibrational modes have been followed through Raman [9, 10] and infrared studies [11, 12]. In the Raman scattering study, Fainstein *et al* [9] report the occurrence of new phonon peaks below the magnetic transition temperature. In addition, they see anomalous hardening of the  $260\text{ cm}^{-1}$  mode, corresponding to the rotations of  $\text{RuO}_6$  octahedra, below  $T_M$ , and this is attributed to spin-dependent scattering. In the IR reflectivity experiments by Boris *et al* [12] and also in the ellipsometric measurements by the same authors [13], correlated shifts to lower frequencies of the Ru-related mode at  $190\text{ cm}^{-1}$  and the mid-IR band at  $4800\text{ cm}^{-1}$  are observed on decreasing the temperature below  $T_M$ . This has been rationalized [12] as arising from the renormalization of the electron–phonon interactions due to the itinerancy of electrons brought about by the onset of ferromagnetic correlations in the Ru–O layer. However, since there is now definitive evidence for AFM ordering [4], it is of interest to take a fresh look at the temperature dependence of IR modes in  $\text{Gd1212}$ .

In this paper we report on the low temperature infrared measurements to probe the behaviour of IR active vibrational modes, particularly across the magnetic transition. We also address the issue of the dependence of IR modes on Cu content. This is motivated by earlier studies by one of the authors [14], wherein doping of copper at the ruthenium site was seen to systematically decrease  $T_M$ , with a corresponding increase in  $T_c$  with a maximum value of 47 K for a dopant concentration of  $\sim 10\%$ . It was of interest to see if the Cu replacement for Ru leads to any changes in the local structure and/or electronic properties that are reflected in the infrared spectrum. With this motivation, room temperature infrared transmission measurements on  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$  samples for  $x = 0.05, 0.1, 0.15$  and  $0.20$  have been carried out and these results are also presented.

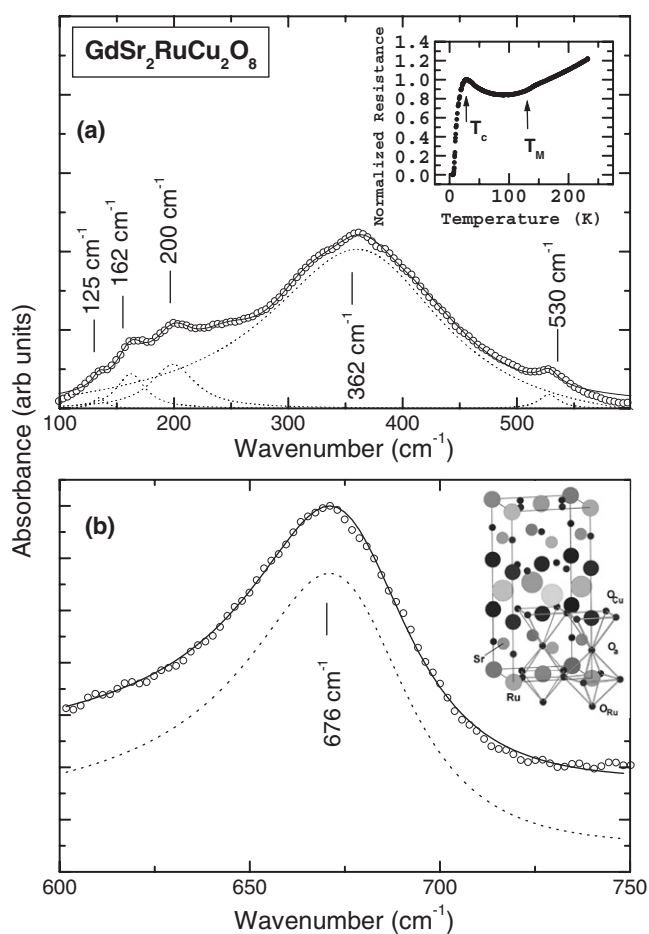
## 2. Experimental details

Samples of  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$ , ( $x = 0.0, 0.05, 0.1, 0.15$  and  $0.20$ ), were prepared by the solid state route and the details of the synthesis and characterization are given in [14]. Infrared absorption measurements were carried out using a BOMEM DA-8 FTIR spectrometer, operating at a resolution of  $4\text{ cm}^{-1}$ . For measurements in the far-infrared over a range of  $30\text{--}600\text{ cm}^{-1}$ , finely ground samples dispersed in HDPE (Reliance Industries Ltd, India), a  $6\text{ }\mu\text{m}$  extended Mylar beamsplitter, Globar source and a DTGS detector were used. For recording spectra in the mid-infrared range, samples dispersed in KBr (Aldrich) matrix, a Ge-coated KBr beamsplitter and an MCT detector were used. Temperature variation ( $300\text{--}10\text{ K}$ ) was carried out using a JANIS continuous flow cryostat and a Lakeshore (DRC-93CA) temperature controller. All the data were analysed by curve-fitting the spectra using BOMEM-GRAMS software and, where necessary, Microcal Origin (version 6.0). Each set of data was subjected to a variety of fitting protocols that included analysis in terms of Lorentzians, Gaussians and Fano lineshape, with two-point as well as multipoint baseline correction, in order to obtain a physically meaningful picture.

## 3. Results and discussion

### 3.1. Infrared absorption measurements on $\text{GdSr}_2\text{RuCu}_2\text{O}_8$

Figure 1 shows the absorption spectra of  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$  measured at 300 K. In the inset of this figure is given the plot of the resistance variation at low temperatures showing the



**Figure 1.** (a) Far infrared absorption spectrum of  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$  measured at 300 K. The solid curve is the fit to a sum of Lorentzians; the components are indicated by the dotted curve. The absorption features at 125, 162, 200, 362 and  $530\text{ cm}^{-1}$  correspond to the  $z$  axis vibrations of Cu, Gd, Ru and oxygen atoms in the  $\text{CuO}_2$  and  $\text{RuO}_2$  planes respectively (see text). The inset shows the temperature dependence of normalized resistance, taken from [14], showing  $T_c$  and  $T_M$ . (b) The asymmetric absorption feature corresponding to the apical oxygen mode; the inset shows the unit cell of  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$ .

magnetic and superconducting transitions with  $T_c \sim 26.5\text{ K}$  and  $T_M \sim 140\text{ K}$  [14]. Also shown is the structure of  $\text{Gd1212}$  having  $P4/mbm$  structure [7]. The FIR part of the spectrum (figure 1(a)) shows phonon features at 125, 162, 200, 362, 530 and  $676\text{ cm}^{-1}$ . A factor group analysis [15] for the  $P4/mbm$  structure, using the information on site symmetries of the atoms from the neutron diffraction study [7], gives  $7A_{2u} + 14E_u$  IR active modes apart from the  $6A_{1g} + 2B_{1g} + 4B_{2g} + 10E_g$  Raman and  $4A_{2g} + 4A_{1u} + 5B_{1u} + B_{2u}$  silent modes. A similar analysis was carried out earlier by Litvinchuk *et al* [11]. Of the above-mentioned IR active modes, the  $A_{2u}$  modes corresponding to the vibrations along the  $z$  axis are predominantly seen owing to the in-plane metallicity of the sample. Comparing the frequencies of occurrence of these vibrational modes with the earlier IR [11, 12] results, the following mode assignments have been made. The  $125\text{ cm}^{-1}$  peak belongs to the Cu vibration, while the  $162\text{ cm}^{-1}$  peak is assigned to the gadolinium mode. The Ru vibration occurs at  $200\text{ cm}^{-1}$ . The mode at

362 cm<sup>-1</sup>, which has the largest oscillator strength, is similar to the oxygen vibration (O<sub>Cu</sub>) in the CuO<sub>2</sub> plane reported by Litvinchuk *et al* [11]. The peak at 530 cm<sup>-1</sup> arises from the vibration of the oxygen atom (O<sub>Ru</sub>) in the ruthenate layer. The highest frequency mode at 676 cm<sup>-1</sup> is due to the apical oxygen (O<sub>a</sub>) vibration. These mode frequencies are in reasonable agreement with earlier results, except that in our study the apical mode is at slightly higher frequency as against 655 cm<sup>-1</sup> reported by Litvinchuk *et al* [11]. We note from figure 1(b) that the apical mode has an asymmetric lineshape, as has also been indicated by Boris *et al* [12]. This part of the spectrum, therefore, has been fitted to a Fano lineshape given by [16]

$$I = I_0 \{1 + [(\omega - \omega_0)/\Gamma q]^2\} / \{1 + (\omega - \omega_0)^2/\Gamma^2\}, \quad (1)$$

where  $\omega$  is the phonon frequency;  $1/q$ , the asymmetry parameter, is a measure of the strength of the coupling between the discrete mode and a continuum, in the present case, of electrons;  $\Gamma$  is the width of the resonance interference between the continuum and the discrete channels. The lineshape of the rest of the phonon modes can be best described by a Lorentzian function. The component modes and the total fit are shown as dotted and solid curves respectively in figure 1.

As the sample is cooled below room temperature, significant changes are observed in the modes corresponding to Ru, O<sub>Cu</sub> and O<sub>a</sub> vibrations as seen from figure 2. We see a hardening of these modes as well as a build-up of intensity in the case of O<sub>Cu</sub> and O<sub>a</sub> modes as the temperature is decreased. These changes are reflected in the mode parameter variations plotted in figure 3 as a function of temperature. In figure 3(a), we see that, as the temperature is decreased, the ruthenium mode frequency is seen to harden. This is opposite to the behaviour seen in the experiments by Boris *et al* [12, 13], wherein an anomalous softening of the Ru mode by about 8%, correlated with the softening of the polaronic band, was observed. Also, in the present experiments, we do not see a distinct polaronic band, and this may be the reason for the different behaviour of the Ru mode. Our measurements are on a sample with a smaller  $T_c \sim 26$  K (as against 45 K in the experiments by Boris *et al*) and this smaller  $T_c$  suggests a lower carrier density, apart from granular effects [17], that may be responsible for the absence of the polaronic feature and thereby account for the observed behaviour of the ruthenium mode. In our investigations, optimum  $T_c$  of 47 K is obtained with Cu doping of 10%.

As a first step to account for the observed hardening of the Ru mode frequency at low temperature, we have tried to analyse this in terms of the cubic anharmonicity model [18], according to which the decay of an optic phonon into two acoustic phonons leads to a temperature dependence of the phonon frequency given by

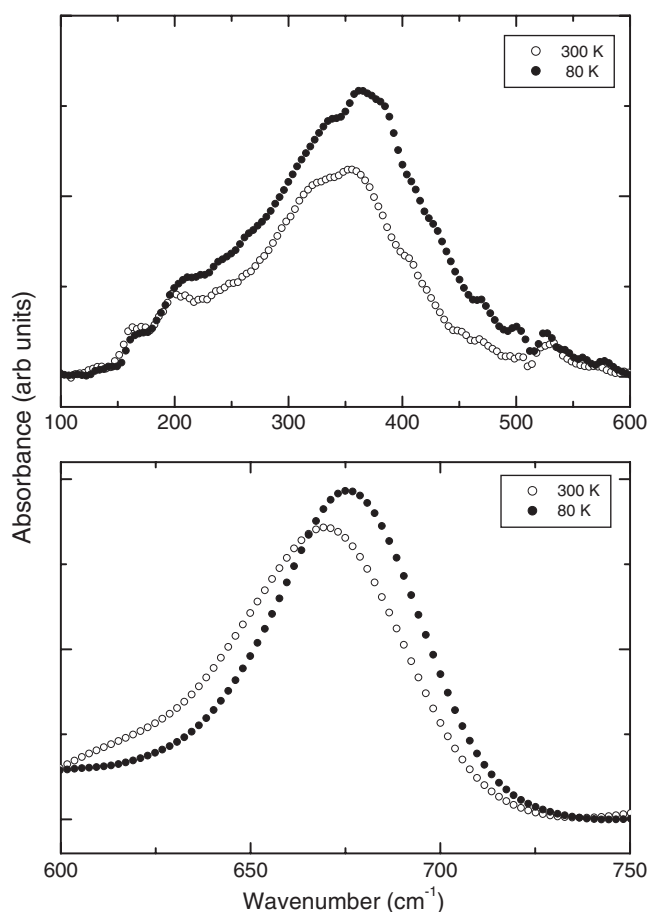
$$\omega(T) = \omega(0) - A_1 [(\exp(\hbar\omega(0)/2kT) - 1)^{-1} + 0.5] \quad (2)$$

where  $\omega(0)$  is the frequency of the phonon mode at 0 K. It is apparent from figure 3(a) that the fit to this model, shown as the dotted curve, is not able to account for the observed frequency variation of the ruthenium mode, in particular, at lower temperatures. It is seen from figure 3(a) that the deviation in the frequency from the anharmonic model starts at around 140–150 K, which also happens to be the temperature close to the magnetic transition. This observation implies that the frequency variation unaccounted for by the anharmonic model, therefore, could be related to the onset of magnetic order among the ruthenium moments. This is made possible by an interaction between the spins and the phonons, first described by Baltensperger [19]. According to this description, when we consider the magnetic exchange energy given by

$$V_{\text{ex}} = -\frac{1}{2} \sum_{ij} J(\mathbf{r}_{ij}) \mathbf{S}(r_i) \cdot \mathbf{S}(r_j), \quad (3)$$

where  $J(\mathbf{r}_{ij})$  represents the superexchange interaction between spins  $i$  and  $j$ , and  $r_{ij}$  is the inter-spin distance; the effect of spin-ordering on the phonon frequency shift, as determined by the second derivative of  $J(\mathbf{r}_{ij})$  with respect to the phonon displacements, is given by

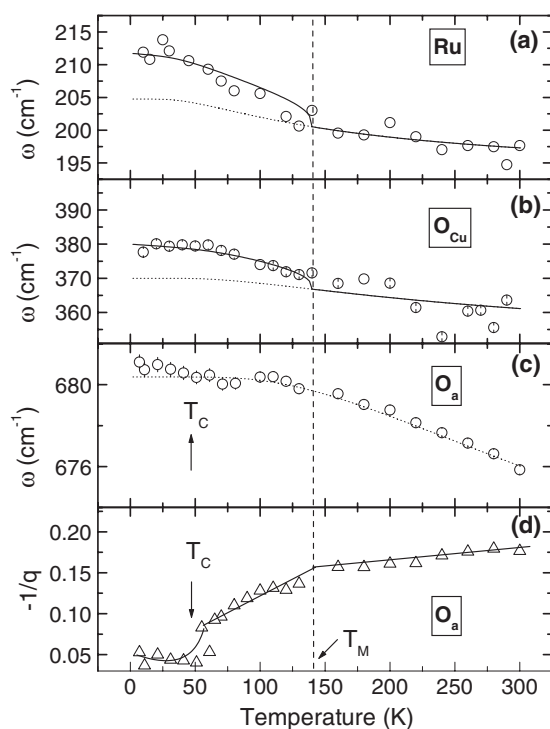
$$A_2 \langle \mathbf{S}(r_i) \cdot \mathbf{S}(r_j) \rangle / S^2, \quad (4)$$



**Figure 2.** Infrared absorption spectra of  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$  at 300 and 80 K. The build-up in intensity and hardening of modes can be clearly seen.

where  $\langle \mathbf{S}(r_i) \cdot \mathbf{S}(r_j) \rangle / S^2$  is the spin correlation function. This term when added to  $\omega(T)$ , as given by equation (2), gives the true frequency variation due to the combined effect of anharmonicity and the spin-phonon interaction [20, 21, 9]. Depending on the sign of  $A_2$ , the spin-phonon interaction may increase or decrease the phonon frequency. Adopting a mean-field description for the spin-correlation function, we have used the functional  $(1 - T/T_M)^\beta$  in equation (4). A model using this mean-field description for the spin correlation function in conjunction with the anharmonic model fits fairly well to the observed frequency variation across  $T_M$  for an exponent value  $\beta \approx 0.35$ , as shown by the solid curves in figure 3(a).

As in the case of the ruthenium mode, the frequency corresponding to the  $\text{O}_{\text{Cu}}$  mode also does not fit well to the anharmonic model below  $T_M$ , as seen in figure 3(b). We know from the structural studies [7, 8] that the O-Cu-O buckling angle decreases with temperature, leading to a shortening of the Cu-O<sub>Cu</sub> bond length. A contraction of the lattice associated with the magnetic transition has been observed in the dilatometric measurements by Fainstein *et al* [22]. While this may account for the hardening of the mode, since the increased hardening of the planar oxygen mode is occurring approximately below the magnetic transition temperature, we have fitted these data using an additional term similar to the one used for the spin-phonon



**Figure 3.** Mode parameter variation with temperature of the (a) Ru, (b) O<sub>Cu</sub> and (c) and (d) O<sub>a</sub> vibrations. The dotted lines correspond to the expected frequency variation based on the anharmonicity model. The solid curves in the top two panels are fits to a model based on the combination of anharmonicity and magnetic interaction as described in the text. The bottom panel (d) shows the variation of the temperature dependence of the Fano asymmetry parameter,  $1/q$ , of the apical oxygen mode. The solid curve shown in the bottom-most panel is a guide to the eye.

interaction of the ruthenium mode. We find, as seen from figure 3(b), that this model fits well to the frequency data. This interesting temperature dependence of the planar oxygen mode suggests that it also responds to changes that are brought about by the ordering of the ruthenium moments.

In contrast to the above observations, the frequency of the apical oxygen mode (figure 3(c)) shows only a marginal increase with the lowering of temperature, as has also been observed by Boris *et al* [12]. This can be well accounted for, down to  $T_c$ , in terms of the anharmonic model, as shown by the dotted curve. Associated with the hardening of the apical mode is the decrease in the Fano lineshape asymmetry parameter ‘ $1/q$ ’ as shown in figure 3(d). The lowering of this asymmetry parameter is accentuated below the magnetic transition temperature and a distinct drop is seen around  $T_c$ . The reduction in the asymmetry parameter points to a reduction in the interaction of this mode with an electronic continuum. It is found that the lineshape of this mode becomes more symmetric in the magnetic phase. This can be attributed to the localization of the carriers due to the antiferromagnetic ordering of the moments, resulting in a decreased metallicity. This point is corroborated by the upturn seen in the resistance versus temperature plot (inset of figure 1(a)) below  $T_M$ . The sudden drop in the ‘ $1/q$ ’ parameter, associated with the superconducting transition, as seen in figure 3(d), has also been seen in other high  $T_c$  compounds such as YBCO [23] and Hg1234 [24] as well as in Rb<sub>3</sub>C<sub>60</sub> [25] below their respective superconducting transition temperatures. This may be due to the condensation

of the electrons in the superconducting state. The reduced interaction of this phonon mode with electrons in the superconducting state should also, through self-energy effects [26], lead to a hardening of the mode. A marginal tendency for this hardening below  $T_c$ , over and above the anharmonic contribution, can be discerned in figure 3(c).

### 3.2. Infrared absorption results on $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$

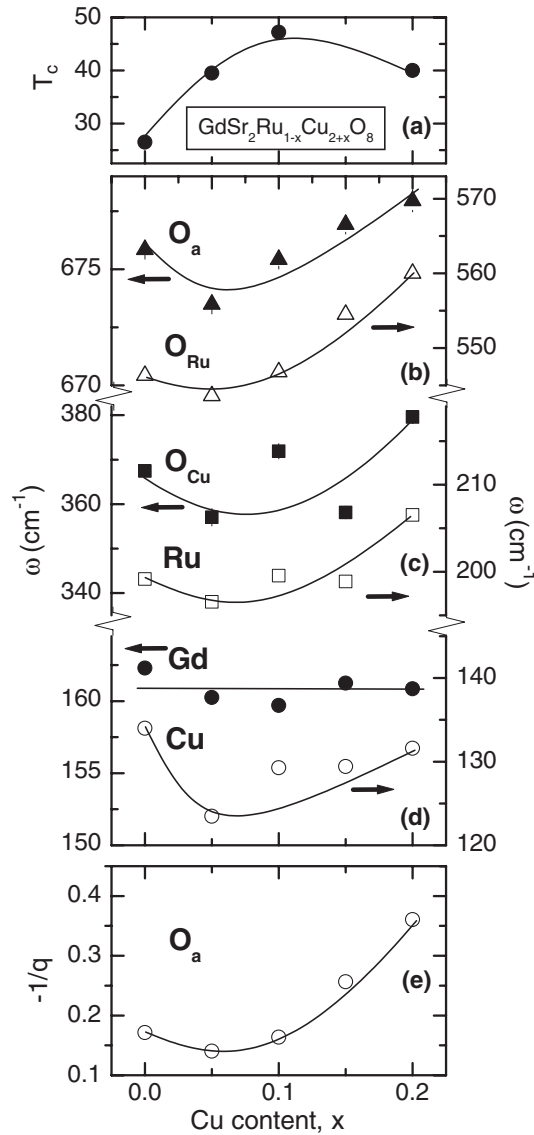
Of the many substitutional studies on  $\text{GdSr}_2\text{RuCu}_2\text{O}_8$  [14, 27–30], a few of them [14, 30] have aimed at studying the dilution of the magnetic lattice. In one such study by Janaki *et al* [14], the effect of dilution of the magnetic lattice has been to decrease the magnetic transition temperature,  $T_M$ , from  $\sim 140$  K in the undoped sample to about  $\sim 125$  K in  $\text{GdSr}_2\text{Ru}_{0.8}\text{Cu}_{2.2}\text{O}_8$ . Correspondingly, the superconducting transition temperature also shows a variation with Cu content, showing a maximum  $T_c$  of  $\sim 47$  K for the sample with  $x = 0.1$  [14]. These results are shown in figure 4(a). In order to understand these variations in terms of changes in local and/or electronic structure, as reflected in the vibrational modes, IR experiments have been done on  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$  samples with  $x$  varying between 0 and 0.20 and these results are summarized in figures 4(b)–(e). It is seen that the Gd mode is unaffected by Cu doping of the Ru site as would be expected based on the crystal structure shown in figure 1(b). The modes corresponding to Cu,  $\text{O}_{\text{Cu}}$ ,  $\text{O}_{\text{Ru}}$  and  $\text{O}_a$  atoms show significant variations and interestingly seem to have a striking similarity with the  $T_c$  versus Cu content [14] shown in the topmost panel.

With Cu replacing Ru, the corresponding bond with  $\text{O}_{\text{Ru}}$  would decrease in length from  $\sim 1.975$  Å towards a value corresponding to the Cu– $\text{O}_{\text{Cu}}$  bond length, namely 1.928 Å [7]. This can account for the significant hardening of the  $\text{O}_{\text{Ru}}$  and Ru modes, as seen in figure 4. The effects of changes in the  $\text{RuO}_2$  plane are also reflected in the neighbouring  $\text{CuO}_2$  plane, as seen in the similar, but smaller changes in the mode frequencies of Cu,  $\text{O}_{\text{Cu}}$  and  $\text{O}_a$ . What is interesting is that these variations are not monotonic, but have a broad minimum centred around  $x \sim 0.1$ . This suggests linkage to the changes brought about by the introduction of holes in the  $\text{CuO}_2$  plane, due to the substitution of Cu for Ru. This should be reflected in the variation of the Fano asymmetry parameter. A plot of the Fano asymmetry parameter,  $1/q$ , versus Cu content for the apical oxygen mode is also shown in figure 4. It is seen that the asymmetry for the apical oxygen shows a broad minimum at  $x \sim 0.1$ . This suggests that the charge transfer to the  $\text{CuO}_2$  plane is maximized for  $x = 0.1$ , the composition for which  $T_c$  shows the maximum.

We have carried out low temperature absorption measurements in the mid-infrared range, across the magnetic transition, in various Cu doped samples. With the lowering of temperature, the apical oxygen mode frequency is seen to harden (figure 5(a)) with a corresponding decrease in width (figure 5(b)). The temperature dependence of the mode frequency is seen to fit well to the anharmonic model (dotted curves in figure 5(a))—as in the case of the undoped sample ( $x = 0$ ). Further, the Fano asymmetry parameter is seen to decrease rapidly below the respective magnetic transition temperatures (figure 5(c)) of the two samples—providing further support for the results presented in figure 3(d). It is interesting to note from figures 5(b) and (c) that with decreasing temperature, there is almost a one-to-one correspondence between the linewidth and the asymmetry parameter,  $1/q$ , even across the magnetic transition.

In order to understand the physical significance, we note that the interaction of the phonon with the continuum of electron states leads to the Fano lineshape as given by equation (1). The same electron–phonon interaction leads to the finite lifetime of the phonons and hence contributes to its width. It can hence be expected that the phonon linewidth ( $\Gamma$ ) and the asymmetry parameter  $1/q$  are related to each other. The Fano asymmetry parameter  $1/q$  is related to the electron–phonon interaction parameter  $V$ , through the relation [31]

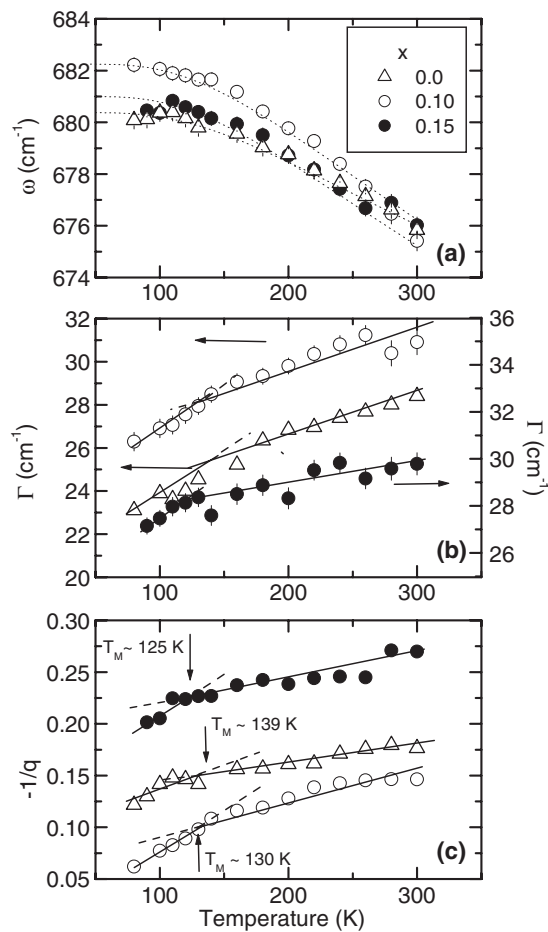




**Figure 4.** (a) Variation of  $T_c$  with copper content in  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$  (from [14]). The compositional dependence of the frequencies of various phonon modes with Cu content is shown in panels (b)–(d). The variation of Fano asymmetry parameter for the apical oxygen atom is shown in panel (e). The mode parameters, obtained from the present IR measurements, seem to correlate with the variation of  $T_c$  with  $x$ . The solid curves are a guide to the eye.

$1/q = \pi\rho VT_e/T_p$ , where  $\rho$  denotes the electronic density of states and  $T_p$  and  $T_e$  are the transition probabilities of the phonon and electronic excitations respectively. The linewidth  $\Gamma$  is related to the electron–phonon interaction through  $\Gamma = \pi\rho V^2$ . This indicates that a plot of  $\Gamma$  versus  $1/q^2$  should result in a linear plot with a slope  $m = T_p^2/\pi\rho T_e^2$ , i.e., inversely dependent on the electron density of states.

This correlation is brought out in figure 6, where  $\Gamma(T)$  is plotted against  $1/q^2(T)$  for both the pure and the doped samples. From the parameters of the linear fits to the curves given

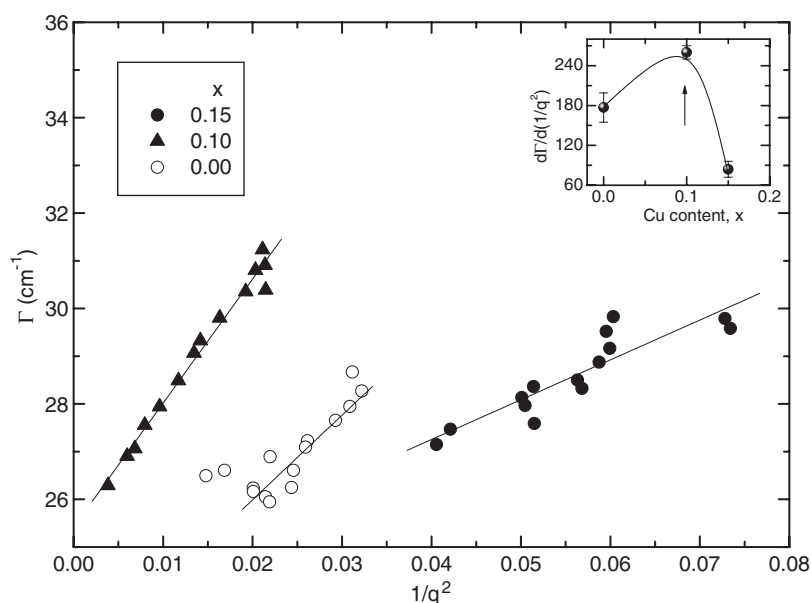


**Figure 5.** Temperature variation of (a) mode frequency, (b) width and (c) the asymmetry parameter of the apical oxygen mode in  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$ , for  $x = 0$  ( $\Delta$ ),  $x = 0.10$  ( $\circ$ ) and  $0.15$  ( $\bullet$ ). The dotted curves in (a) are fits to the cubic anharmonicity model (equation (2) in the text); the solid lines in (b) and (c) are a guide to the eye. The values of  $T_M$  marked in (c) are from [14]. Note the distinct change in the slope of  $1/q$  below  $T_M$ .

in table 1, we observe that while the intercepts of the three plots are more or less the same the slopes show a significant dependence on Cu concentration. This variation, which is shown in the inset, bears a significant similarity to the variation of  $T_c$  with Cu content (see figure 4(a)). The maximum in the slope corresponds to  $x = 0.1$ , which corresponds to minimum electron DOS, as perceived by the apical oxygen, and this corresponds to the optimally doped sample. It is also to be noted that the constancy of the slope even across the magnetic transition (figure 6) implies that no change in the electronic structure occurs as the transition to the magnetic phase takes place.

#### 4. Conclusions

Infrared absorption studies on the temperature and composition dependence of phonon modes in  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$  show several interesting features. With the lowering of temperature, below the magnetic transition temperature, the Ru mode shows an anomalous hardening, over and above that which can be accounted for in terms of anharmonicity, and this can be



**Figure 6.** The variation of the linewidth of the apical oxygen mode with the Fano parameter  $1/q^2$  values obtained from the results of figure 5, in  $\text{GdSr}_2\text{Ru}_{1-x}\text{Cu}_{2+x}\text{O}_8$ , for  $x = 0$  (○),  $x = 0.10$  (▲) and  $0.15$  (●). In the inset is shown the plot of slope versus Cu concentration. Note the similarity in the trend of the curve to  $T_c$  dependence on  $x$  (figure 4(a)).

**Table 1.** Fitted parameters for the  $\Gamma$  versus  $1/q^2$  linear plots for various  $x$ .

Cu concentration, $x$	$m = d\Gamma/d(1/q^2)$	Intercept
0.0	$177 \pm 22$	$22.4 \pm 0.5$
0.10	$260 \pm 10$	$25.4 \pm 0.15$
0.15	$84 \pm 12$	$24 \pm 0.68$

rationalized in terms of spin–phonon interaction. The apical oxygen mode exhibits a Fano asymmetry, with the asymmetry parameter decreasing sharply below the magnetic transition temperature. The asymmetry parameter in various Cu doped samples is seen to be linearly correlated with the linewidth, with a slope that is determined by the carrier density. This slope and composition variation of IR modes, is seen to correlate with the variation of  $T_c$  with Cu content, and points to  $x \sim 0.1$  being the optimally doped sample.

### Acknowledgment

The authors would like to thank Ms T Geetha Kumary for her association in the initial phase of this study.

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