Strong Correlations in $YH_{3-\delta}$ Evidenced by Raman Spectroscopy

A.-M. Racu* and J. Schoenes

Institut für Physik der Kondenbsierten Materie, Technische Universität Braunschweig, Mendelssohnstrasse 3, D-38106 Braunschweig, Germany

(Received 8 July 2005; published 4 January 2006)

Temperature dependent Raman measurements on insulating $YH_{3-\delta}$ thin films are reported. With increasing temperature we observe a huge broadening of a line corresponding to an yttrium mode. This particular mode is assigned to a breathing vibration of the yttrium atoms around an octahedral hydrogen position. The line broadening is discussed in terms of a coupling between this breathing mode and the electron excited from an octahedral H vacancy into the 4*d* conduction band of Y, corroborating the strong correlation models for the electronic structure of YH_3.

DOI: 10.1103/PhysRevLett.96.017401 PACS numbers: 78.30.Hv, 63.20.−e

In 1996 Huiberts *et al.* [1] discovered that yttrium and some other rare-earth films undergo a metal-insulator transition (MIT) when exposed to hydrogen gas. The reversible transition of YH_x from a shiny metal in the dihydride phase ($x = 2$) to a transparent insulator in the trihydride phase ($x = 3$) offers a great potential for practical applications as ''switchable mirror.'' Although various theoretical models have been proposed to describe the MIT, the physics of this phenomenon is still not well understood.

Band structure calculations for an assumed HoD_3 structure, performed prior to 1996 [2,3], predicted a semimetallic character of YH_3, with a large band overlap. After the discovery of the switchable mirrors Kelly *et al.* [4] found that there exists a broken symmetry structure ($P6_3$) whose energy is lower than that of the HoD_3 structure and possesses a gap. The value of the gap was estimated to 0.8 eV and was shown to depend strongly on the position of H in the Y lattice. However, neutron diffraction studies by Udovic *et al.* [5] on powder samples and by Udovic *et al.* [6] and Remhof *et al.* [7] on epitaxial thin films do not corroborate this $P6_3$ broken symmetry structure. Instead, the neutron data are compatible with the $P\bar{3}c1$ and $P6_3$ cm structures. Raman spectroscopy measurements by Kierey *et al.* [8] exclude the centrosymmetric $P\bar{3}c1$ structure and promote the picture of a noncentrosymmetric structure such as $P6_3$ cm. The ^{2}H NMR data by Zogal *et al.* [9] agree very well with the $P6_3$ cm and less with the $P\bar{3}c1$ structure. Thus, experiments clearly favor the $P6_3$ cm structure and do not support the idea that a kind of Peierls instability causes the MIT in YH_x. In this respect it is interesting to note that LaH_x, La-Y alloys [10], and fcc-YH_3 stabilized by MgH_2 [11] switch as well although they retain the fcc structure in the insulating phase. Also recent calculations using the so-called GW approximation [12–14] predict a band gap for YH_3 for all types of crystal structures ($P\bar{3}c1$, $P6_3$ cm, or $P6_3$).

Several groups succeeded to explain the insulating ground state of YH_3 and LaH_3 using strong electron correlations. An important ingredient for the correlation models is the formation of H^{-1} bands. The influence of the H^{-1} lattice on the band structure of YH_3 was described in two different models. Both assume the formation of singlet states, similar to the Zhang-Rice singlet in high-T_c superconductors [15].

Ng *et al.* [16] discuss the band gap in LaH_3 as a result of the narrowing of the H valence band. In this description, LaH_3 is viewed as a Kondo insulator with a large band gap. The removal of hydrogen from the octahedral sites of the insulating LaH_3 introduces vacancies which capture an electron in a donor level. The calculations using the Gutzwiller method estimate for the vacancy state an energy $E_{\mathrm{vac}} = -0.38$ eV below the 5*d* La conduction band. Since the donor levels are quite localized the material becomes metallic only at a very high doping level of about 20% vacancies.

Eder *et al.* [17] introduce a further aspect in their model. In contrast to the model of Ng *et al.*, the MIT is explained by a shift of the H band, with the retention of the bandwidth. The correlation effects are a consequence of the large change in the H 1*s* orbital radius upon orbital occupation. This leads to the formation of localized singlet-bound states involving one electron on the hydrogen and one electron on the metal orbitals.

There are several experiments confirming that hydrogen in YH_3 behaves like a negative ion, and some which hint to strong electron correlations. Electromigration experiments support the idea of negatively charged hydrogen in YH_3 [18]. Infrared Fourier transform measurements by Rode *et al.* [19] determine a significant charge transfer from yttrium to hydrogen of approximately 0.5 e^- per hydrogen atom. Electrical conductivity data of Hoekstra *et al.* [20] and Roy *et al.* [21] over a wide temperature and hydrogen concentration range both in the metallic and insulating phases collapse onto a universal curve with unusually large critical exponents, pointing to the important role played by electron correlations. Angular resolved photoemission spectroscopy data for YH_3 by Hayoz *et al.* [22] have also been interpreted in terms of a strongly correlated electron system. Furthermore, the Fermi-surface topology of rare-earth dihydrides determined by Koitzsch *et al.* [23] can be

described in a model involving the octahedral hydrogen atoms and relates to the scenarios of Eder *et al.* and particularly Ng *et al.* Yet, these experimental methods are all indirect, calling for further and possibly more direct evidence for the correlated models. Raman spectroscopy has proven recently to be a powerful method to evidence correlations in high-T_c superconductors [24] raising the intriguing question whether this method can also shed light on the electronic structure and the MIT of switchable mirrors.

In this Letter, we present the results of a study of the temperature dependence of the linewidths of several Raman phonon lines of $YH_{3-\delta}$. The most striking effect is the broadening by a factor of almost 6 between 5 and 300 K of a particular mode, which is assigned to a breathing vibration of the yttrium atoms. This huge line broadening is attributed to a coupling of the breathing mode to electrons excited from a H vacancy into the 4*d* conduction band of Y, in direct support of the strong correlation model of Ng *et al.* [16].

Thin yttrium films have been grown by molecular beam epitaxy on (111) CaF_2 substrates [25]. The base pressure during the deposition was lower than 1×10^{-9} mbar. The quality of the yttrium film was monitored *in situ* by reflection high energy electron diffraction. To protect the yttrium films against oxidation and to support the hydrogenation process, the films were covered with 10 nm thick Pd layers, deposited at room temperature. The samples were loaded in a gas cell with H_2 at a pressure of 1 bar. The films are transparent, evidencing that the hydrogen content is over 2.75 [26]. Yet, since stoichiometric YH_3 is only reached above 4 GPa [27] our samples are expected to contain a substantial number of vacancies which act as donors and we write $YH_{3-\delta}$.

Raman spectra have been recorded using a commercial micro-Raman spectrometer (Jobin Yvon LabRam HR), operated with a notch filter and a grating monochromator. All samples were measured through the transparent CaF_2 substrate, from the back side, in order to avoid losses due to absorption of Pd. The temperature dependent measurements were performed using a CryoVac cryostat type Micro between 4 K and 320 K.

A series of temperature dependent Raman spectra of a $YH_{3-\delta}$ sample is shown in Fig. 1(a). The CaF_2 substrate gives the main feature in all the spectra at 322 cm^{-1}. For clarity, the spectra are displaced, adding a constant factor to the intensity. Previous measurements performed by Kierey *et al.* [8] on isotope exchanged samples revealed for each line which atoms vibrate. With the exception of the lines 1 and 2 below 200 cm^{-1}, all lines are shifted by approximately $\sqrt{2}$ if hydrogen is replaced by deuterium. This indicates that the low frequency modes (1 and 2) involve vibrations of Y only, while the other lines correspond to vibrations including hydrogen or deuterium. The same authors presented a complete polarization and angular dependence study of the intensity for the Raman active modes in YH_3, determining the symmetry of these modes. Thus, the modes 2 to 7, 9, and 10 have A_1 symmetry, while the modes 1, 8, and 11 have E symmetry.

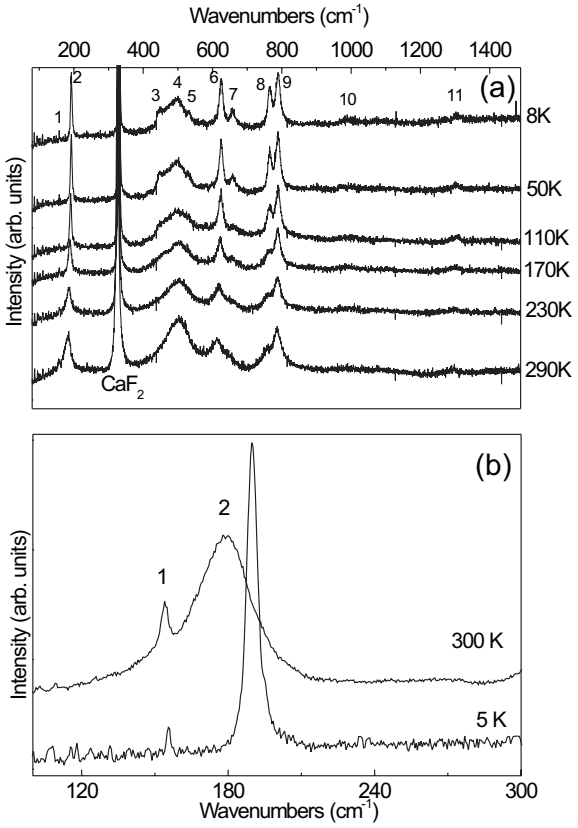

FIG. 1. (a) Temperature dependent Raman measurements for $YH_{3-\delta}$. (b) Enlarged view of the two lines belonging to yttrium vibrations.

There is a substantial decrease of the phonon linewidth with decreasing temperature. As a consequence, two more peaks around 500 cm^{-1} are visible in the $YH_{3-\delta}$ spectrum as the temperature is lowered [the upper spectra compared to the lower spectra in Fig. 1(a)]. These correspond to A_1 symmetry vibrations of the hydrogen atoms. The line shapes of the $YH_{3-\delta}$ peaks were fitted by Lorenzian functions with full width at half maximum (FWHM) Γ. The values of Γ depend on the decay mechanism of phonons. The most common process is a decay of the optical phonon into two longitudinal acoustic modes, a process which was intensively studied and which can be described with perturbation theory [28]. Another possible decay mechanism of phonons is electron-phonon coupling. It has been shown in some superconducting materials [29] and Kondo insulators [30] that the ratio Γ/ω_0 for a particular mode is a direct estimate of that phonon's contribution to the electron-phonon coupling parameter, and is given by

$$\Gamma/\omega_0 = \pi N(0)\hbar\omega_0\lambda. \quad (1)$$

Here $N(0)$ is the electronic density of states at the Fermi surface and λ is its contribution to the electron-phonon coupling parameter. The important conclusion drawn from Eq. (1) is that the broadening of a phonon line due to electron-phonon coupling is a measure of the free carrier concentration in the sample.

A large band width renormalization ratio, caused by the opening of a superconducting gap, was exploited by Axe and Shirane to estimate electron-phonon coupling strengths in Nb_3Sn [29]. Nyhus *et al.* [30] and Menzel *et al.* [31] observed a similar effect for several Raman active lines of FeSi, which is sometimes claimed to be a strongly correlated material, i.e., a Kondo insulator.

In the following we will demonstrate that line 2 near 180 cm^{-1} displays an anomalous temperature dependence. To do so we will first compare the temperature dependence of the line width of line 1 and 2 corresponding to Y vibrations and then with the other lines involving hydrogen. Since line 1 is barely seen in the full spectra [Fig. 1(a)] we show in Fig. 1(b) an enlarged view of the low energy range with a higher integration time. One recognizes clearly that line 2 broadens considerably with temperature while line 1 broadens only very little. Figure 2 presents the normalized damping ratio Γ/ω_0 as function of temperature for the 2 modes. For line 2 we find a ratio Γ/ω_0 of 14% at room temperature compared to only about 1.5% for line 1 at 155 cm^{-1}. The lines above 400 cm^{-1} which correspond to hydrogen vibrations are broader than line 1. However, the effect is reduced when the width is normalized to the frequency and, more significantly, the temperature dependence is similar to that of line 1 and completely different from line 2 (see as an example line 9 in Fig. 2). The larger linewidth of the hydrogen vibrations is attributed to the lower mass of hydrogen and the presence of hydrogen vacancies.

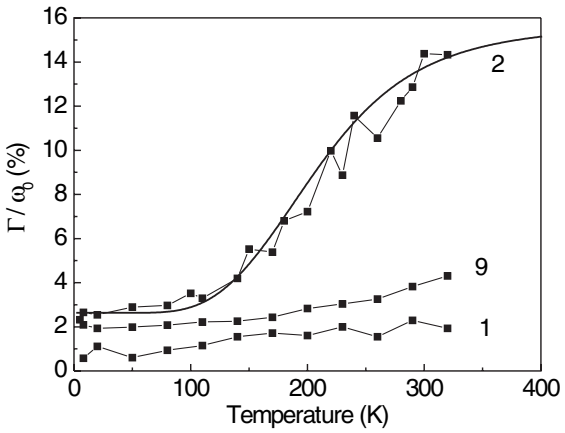

FIG. 2. The phonon linewidth Γ divided by the phonon frequency ω_0 for the two yttrium vibration modes and for one hydrogen line in $YH_{3-\delta}$. The solid line is a fit using Eq. (2), as explained in the text.

Thus the temperature dependence of the linewidth of the lines 1 and 3 to 11 is normal and can be attributed to phonon-phonon relaxation. To account for the anomalous broadening of line 2 we need some additional mechanism and we propose electron-phonon coupling. The question which arises, then, is which electrons can produce such a strong electron-phonon contribution in the wide-gap insulator YH_3. Before answering this question, it is also important to note that such a huge broadening is unique for the insulating $YH_{3-\delta}$ phase. Indeed, previous experiments revealed that in metallic $YH_{2+\epsilon}$ the two vibration modes of the Y atoms display a normal behavior [32].

In the strong correlation model of Ng *et al.* [16] for the similar compound LaH_3 an octahedral hydrogen vacancy captures an electron which can be thermally excited into the $5d$ conduction band of lanthanum. This vacancy state acts as a donor and is estimated to sit at an energy $E_{\mathrm{vac}} = -0.38$ eV below the conduction band. We propose that the thermally excited electrons from this donor state couple with the phonon, inducing a broadening of the phonon line. The concentration of thermally excited carriers in the conduction band as a function of temperature can be estimated using the model of a doped semiconductor [33]:

$$N(T) = \frac{2N_D}{1 + \sqrt{1 + 4\frac{N_D}{N_C}\exp(E_d/kT)}}. \qquad (2)$$

In Eq. (2), N_D represents the density of hydrogen vacancies and N_C is the density of states in the conduction band, which depends on the temperature as $T^{3/2}$. Using Eqs. (2) and (1) and neglecting the phonon-phonon interactions, the line broadening of the mode 2 of $YH_{3-\delta}$ has been fitted. In Fig. 2 the solid line represents the result of the fit. We find a good agreement with the temperature dependence of the line broadening for an activation energy $E_d \approx 0.1$ eV. This energy is reasonably close to the rather rough estimate of 0.38 eV of Ng *et al.* [16] for LaH_3.

After the electron is excited from the octahedral vacancy site, it will occupy the lowest Y $4d$ orbitals in the conduction band. In the hexagonal YH_3 structure the coordination of the yttrium atoms is tetrahedral and not octahedral as is the case of LaH_3 which was discussed by Ng *et al.* Therefore, the lowest $4d$ conduction band of YH_3 has e_g character (and not t_{2g}, as in LaH_3). Wang and Chou [2] have shown that there exists a strong overlap of the e_g subbands formed by Y $4d$ $3z^2$-r^2 orbitals with H $1s$ orbitals. The vibration mode of the line 2 of $YH_{3-\delta}$ is illustrated in Fig. 3. This mode has A_1 symmetry and corresponds to a breathing of the Y atoms around the octahedral hydrogen position. During such a vibration the overlap between the e_g orbitals oscillates, allowing for a strong coupling between the breathing mode and the excited electron. In contrast, in the vibration of line 1 two groups of opposite yttrium atoms perform opposite scissor oscillations, causing no change in the overlap of the e_g orbitals.

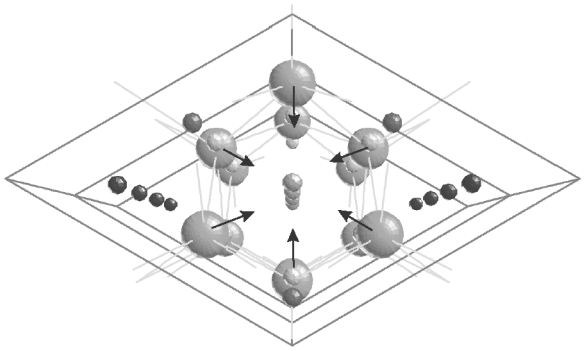

FIG. 3. A_1 breathing mode of YH_3 in $P6_3$ cm space group. The big circles are the yttrium atoms; the small circles are the tetrahedral and octahedral coordinated hydrogen atoms. The arrows show the displacement of the yttrium atoms around an octahedral hydrogen position in the A_1 vibration mode.

In conclusion, temperature dependent Raman scattering measurements on $YH_{3-\delta}$ films reveal for one particular breathing mode of the yttrium atoms a huge line broadening with increasing temperature. This effect is attributed to the decay of the phonon via electron-phonon interactions. A model is presented which relates the latter to the excitation of electrons from a donor level just below the conduction band edge. The data strongly support the correlated electron theory proposed by Ng *et al.* [16] for the metal-insulator transition in YH_x.

We wish to thank G. Zwicknagl and M. Rice for fruitful discussions.

Note added.—After completing this work we performed measurements above 320 K and we observed that the width of line 2 saturates, corroborating the key assertion of our model.

*Electronic address: a.racu@tu-bs.de

[1] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature (London) **380**, 231 (1996).
[2] Y. Wang and M. Y. Chou, Phys. Rev. B **51**, 7500 (1995).
[3] J. P. Dekker, J. van Ek, A. Lodder, and J. N. Huiberts, J. Phys. Condens. Matter **5**, 4805 (1993).
[4] P. J. Kelly, J. P. Dekker, and R. Stumpf, Phys. Rev. Lett. **78**, 1315 (1997).
[5] T. J. Udovic, Q. Huang, and J. J. Rush, J. Phys. Chem. Solids **57**, 423 (1996).
[6] T. J. Udovic *et al.*, Phys. Rev. B **61**, 12 701 (2000).
[7] A. Remhof, G. Song, Ch. Sutter, A. Schreyer, R. Siebrecht, H. Zabel, F. Güthoff, and J. Windgasse, Phys. Rev. B **59**, 6689 (1999).
[8] H. Kierey, M. Rode, A. Jacob, A. Borgschulte, and J. Schoenes, Phys. Rev. B **63**, 134109 (2001).
[9] O. J. Zogal, W. Wolf, P. Herzig, A. H. Vuorimäki, E. E. Ylinen, and P. Vajda, Phys. Rev. B **64**, 214110 (2001).
[10] A. T. M. van Gogh *et al.*, Phys. Rev. B **63**, 195105 (2001).
[11] S. J. van der Molen *et al.*, Phys. Rev. B **63**, 235116 (2001).
[12] T. Miyake, F. Aryasetiawan, H. Kino, and K. Terakura, Phys. Rev. B **61**, 16 491 (2000).
[13] P. van Gelderen, P. A. Bobbert, P. J. Kelly, G. Brocks, and R. Tolboom, Phys. Rev. B **66**, 075104 (2002).
[14] J. A. Alford, M. Y. Chou, E. K. Chang, and S. G. Louie, Phys. Rev. B **67**, 125110 (2003).
[15] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, R3759 (1988).
[16] K. K. Ng, F. C. Zhang, V. I. Anisimov, and T. M. Rice, Phys. Rev. B **59**, 5398 (1999).
[17] R. Eder, H. F. Pen, and G. A. Sawatzky, Phys. Rev. B **56**, 10 115 (1997).
[18] S. J. van der Molen, M. S. Welling, and R. Griessen, Phys. Rev. Lett. **85**, 3882 (2000).
[19] M. Rode, A. Borgschulte, A. Jacob, C. Stellmach, U. Barkow, and J. Schoenes, Phys. Rev. Lett. **87**, 235502 (2001).
[20] A. F. Th. Hoekstra *et al.*, Phys. Rev. Lett. **86**, 5349 (2001).
[21] A. S. Roy, A. F. Th. Hoekstra, T. F. Rosenbaum, and R. Griessen, Phys. Rev. Lett. **89**, 276402 (2002).
[22] J. Hayoz, C. Koitzsch, M. Bovet, D. Naumovic, L. Schlapbach, and P. Aebi, Phys. Rev. Lett. **90**, 196804 (2003).
[23] C. Koitzsch *et al.*, Phys. Rev. B **70**, 165114 (2004).
[24] J. Bäckström *et al.*, Phys. Rev. B **61**, 7049 (2000).
[25] A. Borgschulte, S. Weber, and J. Schoenes, Appl. Phys. Lett. **82**, 2898 (2003).
[26] M. Kremers *et al.*, Phys. Rev. B **57**, 4943 (1998).
[27] A. R. Wildes, R. C. C. Ward, M. R. Wells, and B. Hjörvarsson, J. Alloys Compd. **242**, 49 (1996).
[28] J. Jimenez, E. Martin, A. Torres, and J. P. Landesman, Phys. Rev. B **58**, 10 463 (1998).
[29] J. D. Axe and G. Shirane, Phys. Rev. Lett. **30**, 214 (1973).
[30] P. Nyhus *et al.*, Phys. Rev. B **51**, R15626 (1995).
[31] D. Menzel, M. Finke, T. Donig, A.-M. Racu, and J. Schoenes (to be published).
[32] A.-M. Carsteanu, M. Rode, D. Zur, A. Borgschulte, H. Schröter, and J. Schoenes, Phys. Rev. B **69**, 134102 (2004).
[33] H. Ibach and H. Lüth, *Festkörperphysik* (Springer Lehrbuch, New York, 1995), 4th ed.