Journal of Alloys and Compounds 293–295 (1999) 334–337

Dynamics of hydrogen in scandium and yttrium by acoustic spectroscopy

F. Trequattrini[a,*], G. Cannelli[b], R. Cantelli[a], F. Cordero[c], O. Florêncio[d]

[a]Dipartimento di Fisica, Università di Roma 'La Sapienza', I-00185 Roma, Italy and INFM, Italy
[b]Dipartimento di Fisica, Università della Calabria, Arcavacata di Rende (CS), I-87039 Cosenza, Italy and INFM, Italy
[c]CNR, Area di Ricerca di Tor Vergata, Ist. di Acustica 'O.M. Corbino', 00189 Roma, and INFM, Italy
[d]Universidade Federal de São Carlos, Departamento de Fisica, C. P. 676, 13.565-905 São Carlos-S.P., Brazil

Abstract

Acoustic spectroscopy has been employed to investigate the nature of the processes occurring at liquid He temperature in pure polycrystalline Y and Sc for frequencies in the kHz range. The anelastic spectra indicate that hydrogen is delocalized in at least two different tunnel systems. Possible tunnel systems are discussed: the isolated or interacting H atom tunnelling between pairs of adjacent tetrahedral sites, the H atom tunnelling near single or paired O traps. It is concluded that, in the present dilute alloys, the observed relaxations have to be attributed to tunnel systems constituted by H trapped by O displaying transition rates governed by the multiphonon process. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Point defects; H tunnelling; Anelasticity

1. Introduction

Various experiments in hcp rare-earth metals [1–15] have revealed effects associated to the dynamics of hydrogen consisting of slow and fast local motions on at least three different regimes of mobility. The slow motion, characterised by an activation energy of 0.6 eV, is identified with long-range diffusion and H pair dissolution/formation [7,8,13], as observed by Gorsky effect [1], quasielastic neutron scattering QNS [2–4], nuclear magnetic resonance (NMR) [5,6] and acoustic spectroscopy [7–9]. Another aspect of the slow motion is also the reorientation of H around oxygen impurities, which occurs with an activation energy of 0.15 eV as observed by acoustic spectroscopy [9–12]. Instead, fast motion of hydrogen involves local tunnelling between adjacent tetrahedral sites (transition rates included between 10^4 and 10^7 s^{-1} in the temperature range 10–100 K) as revealed by NMR [14,15] and anelastic spectroscopy [9–12]. Besides, ultra fast motion (10^{10} and 10^{12} s^{-1}, between 10 and 200 K) has been observed over the same temperature range by QNS [2,4]. Both fast and ultra fast motion can be fairly interpreted, using the two-level systems (TLS) formalism, in terms of local tunnelling of H between pairs of adjacent tetrahedral sites (T) along the c-axis. On such pairs which can be occupied by no more than one atom, hydrogen delocalizes in TLS [9–12,14,15]. The reason why the same types of sites give rise to so different relaxation rates can be justified with the different types of tunnel systems: the isolated non interacting H atom, the H atom elastically interacting with other H atoms or with an heavy interstitial impurity, such as oxygen. What distinguishes these tunnel systems is the asymmetry between the wells which determines the electron- and phonon-induced transition rates and the intensity of the relaxation: the larger the asymmetry is, the smaller is the transition rate. Up to now most experiments have been conducted on highly hydrogenated alloys (>1 at% H) where the role of trapping impurities is negligible. Instead, distinct relaxation processes due to H hopping and tunnelling near a trapping impurity have already been observed in dilute Y–H system [9,12]. In order to investigate the nature of the tunnel systems in rare earths and clarify the role played by the heavy trapping centres on the formation of hydrogen tunnel systems, we have conducted a study of anelastic spectroscopy. It was performed down to liquid helium temperatures on pure polycrystalline scandium and yttrium containing a few thousands of at ppm H and some hundreds of at ppm O+N+C.

2. Experiments

The samples were two rectangular bars of pure poly-

---

*Corresponding author.

0925-8388/99/$ – see front matter
PII: S0925-8388(99)00393-X

crystalline Sc (~50×1.4×6.1 mm^3) and one of pure polycrystalline Y (40×4.4×2 mm^3), purchased from the Ames Laboratory. The gaseous impurities of the samples in the 'as received state' were: 849 at ppm H, 380 at ppm O+N+C, residual resistivity ratio ($R_{273\ K}/R_{4\ K}$), RRR=50 for Sc; 880 at ppm H, 600 at ppm O+N, residual resistivity ratio RRR=34 for Y. During the experiments, the possible variations of the interstitial impurities were monitored by considering separately the values of the electrical resistivity at 4.2 and 273 K instead of the RRR values which are affected by the hydrogen clustering (H–H pairs, *m*O–*n*H complexes) occurring below 200 K.

Before every thermal treatment, the surface oxide was abraded immersed in CCl_4 by emery paper, in order to reduce the O contamination; then the samples were wrapped in zirconium foils, with a Mo wire preventing the contact with the foils, and annealed at 1000 K in UHV (10^{-8} mbar range); finally they were cooled to room temperature in less than 4 min.

The anelastic spectroscopy measurements (Q^{-1}) were carried out between 1 and 300 K, on cooling/heating at rates included between 0.5 and 2 K/min by electrostatically exciting the samples on different flexural vibration modes with frequencies in the kHz range.

3. Results and discussion

The relaxation spectra below room temperature of polycrystalline yttrium and scandium in the 'as received state' are shown in Fig. 1. All measurement runs have been performed during cooling.

A previous investigation carried out by us revealed six thermally activated processes in Y. Those processes, reproduced in the present sample ($\rho_{4\ K}=1.6$ μΩ cm, $\rho_{273\ K}=60.9$ μΩ cm, RRR=38), have been interpreted as follows: P6 around 280 K is the well known relaxation to due the formation/dissolution of H pairs [7,8,13]; P5 around 210 K is caused by a mechanism involving interstitial hydrogen dragged by dislocations [12]; P4 and P3 are ascribed to the local motion of H trapped by the oxygen atoms [9,12]; finally, below 50 K, processes T1 and T2 present features indicative of quantum-mechanical tunnelling of hydrogen [9–12]. The mechanisms of P3 and P4 can be inferred from the phenomenology systematically observed during cooling/heating runs, after H-, O-dopings and after H outgassing. Peak P4 is associated to the O–H complex unstable down to the liquid nitrogen temperature. Its intensity can be reduced either with increasing the H content (above 1 at% H), due to the saturation and the blocking of the trap sites around O, or by the depletion of the O–H population with proceeding the H outgassing. Peak P3, more pronounced in samples with higher O-content, displays a similar behaviour and should be attributed to a different type of cluster, likely the 2O–H complex (in the present sample with less than 600 at ppm O, it is hardly detectable around 90 K).

The anelastic spectrum of Sc exhibits thermally activated relaxations less intense but similar to those reported in Y, thus we use the same labels P6, P5, ... T1, T2 to indicate the corresponding peaks. In the 'as received' state (Sc, curve 1, $\rho_{4\ K}=0.98$ μΩ cm, $\rho_{273\ K}=48.5$ μΩ cm), P4 and P3 are absent. This can be explained with the higher purity of the material: we suppose that the trap sites (380 at ppm O+N+C) are saturated by more than one H atom (849 at ppm H or even more, as shown later) and that the hopping of H in higher order complexes is inhibited. Curve 2 displays the Sc spectrum after heating up to 480 K in about 3 h in high vacuum (~10^{-7} mbar). This thermal treatment does not produce any O contamination and H outgassing because the values of resistivity ($\rho_{4\ K}=1.03$ μΩ cm, $\rho_{273\ K}=49.5$ μΩ cm), and the intensity of peak P6 does not change within experimental errors. In spite of this

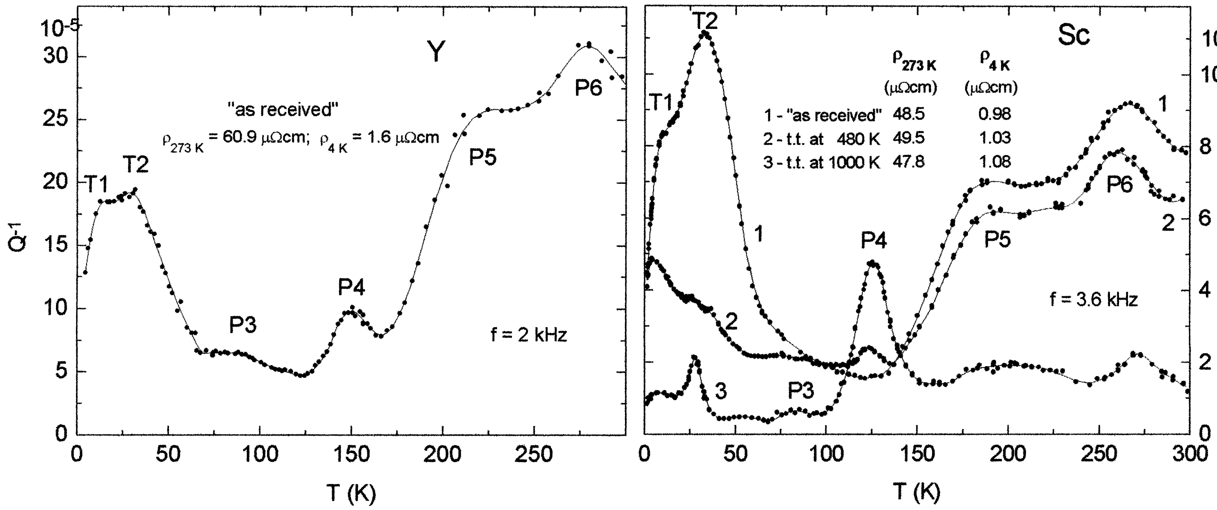

Fig. 1. Anelastic relaxation spectra of Y, and Sc after subsequent thermal treatments (t.t.).

fact, the intensity of processes T2 was markedly reduced. An explanation of this behaviour may be a different clustering of hydrogen consequent to a variation of the state in solid solution of the trapping centres (mainly oxygen). If we suppose that, similarly to hydrogen, oxygen may form stable pairs, we would expect a difference in the concentration of the H, H–H, O–H and O–O–H populations between the 'as received' material and its state after the ageing at 480 K. In particular, the equilibrium values of the concentration ratio C_O/C_{O-O} is expected to be an increasing function of temperature. Therefore, if during the material preparation a smaller C_{O-O} concentration had frozen by rapid cooling from high temperature, the O–O population should have increased during the 480 K. We have shown that at this temperature O is mobile in Y, so that the equilibrium concentration of the O pairs can be reached in a short time [12]. The possibility of oxygen precipitation is excluded because the phase diagram of the Sc–O system shows that O concentration in solid solution is of the order of some at% down to room temperature [16]. In addition, O precipitation would cause a much larger drop than O pairing and no significant variation of resistivity was observed.

From the above considerations we infer that the relaxing entities which give rise to peaks T1 and T2 are formed by O–O–H and O–H complexes, respectively. In fact, the 480 K ageing increased the O–O population at the expenses of the O population, without changing the total H concentration. Therefore, the O–H population is decreased and more H atoms are available for the O–O–H and the untrapped H populations. Neither T1 nor T2 are due to untrapped H, since none of them increase from curve 1 to curve 2. Instead, peak T2 should be due to O–H complexes as demonstrated by its marked reduction, while peak T1 whose intensity is little affected should be due to O–O–H complexes.

The annealing treatment at 1000 K (curve 3, $\rho_{4\ \mathrm{K}}=1.08$ μΩ cm, $\rho_{273\ \mathrm{K}}=47.8$ μΩ cm) produces: (i) a H outgassing deduced from the reduction of P6 and P5, and from the resistivity decrease $\Delta\rho_{273\ \mathrm{K}}=0.7\div1.7$ μΩ cm indicating that $0.2\div0.4$ at% H was contained in the as received sample (assuming the value of 4 μΩ cm/at% H [13] for the specific resistivity); (ii) a light O contamination revealed by the resistivity increase $\Delta\rho_{4\ \mathrm{K}}=0.1$ μΩ cm; (iii) the appearance of P4 (and perhaps of P3 around 80 K) due to reduced blocking effect of H.

Though processes T1 and T2 display relaxation rates ($\tau^{-1}=10^4\ \mathrm{s}^{-1}$ in Y, $\tau^{-1}=2\ 10^4\ \mathrm{s}^{-1}$ in Sc, around 30 K) lower than those found by QNS [2,4], NMR [14,15], and ultrasonic attenuation [10,11] experiments, nevertheless they have to be associated with H tunnelling. In fact, if interpreted in terms of a classical over-barrier hopping, the shift of the peak temperature with frequency would indicate an activation energy lower than 50 meV with an attempt frequency of the order of 10^{-11} s. These values of energies appear to be unphysical because are even lower than the energy of the first excited state for H vibration in the *T* sites as deduced from neutron scattering in Y and Sc [17–19]. In order to explain how tunnelling between pairs of adjacent *T* sites can give rise to so different relaxation rates, different types of tunnel systems has to be distinguished: the isolated H atom, the H pair along the *c*-axis and the atom H trapped by an O atom. The major difference among these types of adjacent *T* sites is the asymmetry *a* between the two potential wells, and possibly also the tunnelling matrix element *t*. This difference determines the transition rates, which in the two-level model (TLS) are proportional to $\left(\frac{t}{E}\right)^2$ where $E=\sqrt{t^2+a^2}$ is the energy separation between the levels. Therefore, the larger is the asymmetry, the smaller is the transition rate. In the QNS experiments the transition rates are estimated from the inverse of the width of the quasi-elastic peak, thus the ultra fast TLS's are better detected and can be identified with single H atoms in nearly symmetric pairs of sites [2,4]. Instead, the present acoustic measurements characterised by the lower rates would rule out the symmetric tunnel systems though we do not exclude they might manifest themselves at temperatures lower than those here explored.

Possible asymmetric tunnel systems that remain to consider are: (i) H atoms whose interaction generates the asymmetry on the adjacent *T* sites, (ii) the trapped H on the *m*O–*n*H complexes where a strong asymmetric distortion of the two potential wells can be caused by the trapping impurity [9]. In the as received state (curve 1, Sc), processes T1 and T2 could presumably derive from the superposition of both types of tunnel systems but the previous considerations exclude a contribution from the untrapped H. Then we conclude that T2 is associated to a TLS within the O–H complex and T1 within the O–O–H complex. The reason why the untrapped H should not give any contribution to the relaxation at this temperature is that due to the low concentration (less than 0.2 at% H) the H interaction does not significatively affect the symmetry of the the tunnel systems. The relaxation spectrum after the 1000 K annealing confirms the hypothesis of TLS associated to the trapping centres. In fact, T1 and T2 are still present when the untrapped H population is strongly reduced (P6 is nearly suppressed) and the *m*O–*n*H population complexes is becoming predominant. The fact that in this state T2 is more intense than T1 (curve 3) can be again explained by a new redistribution of the O and O–O populations, with $C_O > C_{O-O,}$ frozen by the rapid cooling from the high temperature annealing.

Fig. 2 presents the shift of relaxation curves T1 and T2 in the as received Sc carried out concomitantly at two different resonance frequencies. In terms of the TLS formalism the energy loss Q^{-1} associated to each relaxation curve T1, T2 is given by:

$$Q^{-1}=\Delta_R\frac{\omega\tau}{1+(\omega\tau)^2} \qquad (1)$$

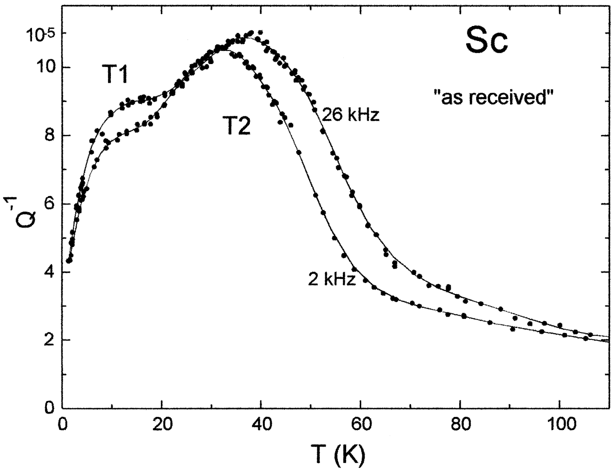

Fig. 2. Temperature shift of T1 and T2 in Sc with frequency.

$$\Delta_R \propto \frac{c\,\Delta\lambda^2}{k_B T}\,\mathrm{sech}^2\left(\frac{E}{2k_B T}\right) \tag{2}$$

where $\omega = 2\pi f$ is the angular frequency, $\tau(T)$ the relaxation time; Δ_R is the relaxation strength which is proportional to the concentration c of the relaxing entity and to the square of the change $\Delta\lambda$ of the long range part of the local elastic distortion. In relation (1) the Debye function is maximum at $\omega\tau = 1$ and the relaxation time $\tau(T)$ describes the type of interaction of the tunnel system with the environment, i.e. electrons and phonons. In our case due to the high dilution of the impurities (H, O), a distribution of the energy separation is not required. The resulting relaxation rate is $\tau^{-1} = \tau_{\mathrm{el}}^{-1} + \tau_{\mathrm{1ph}}^{-1} + \tau_{n\mathrm{ph}}^{-1}$ considering the electrons-, one phonon- and multiphonon-coupling, respectively. The corresponding expressions are:

$$\tau_{\mathrm{el}}^{-1} = \left(\tau_0^{-1}\right)_{\mathrm{el}} \coth\left(\frac{E}{2k_B T}\right) \tag{3}$$

in the normal state, and

$$\tau_{\mathrm{1ph}}^{-1} = \left(\tau_0^{-1}\right)_{\mathrm{1ph}} \coth\left(\frac{E}{2k_B T}\right);$$

$$\tau_{n\mathrm{ph}}^{-1} = \left(\tau_0^{-1}\right)_{n\mathrm{ph}} \left(\frac{E}{2k_B T}\right)^n \tag{4}$$

The analysis of the present results is in progress and will be published as the second part of the present investigation. However, some qualitatively considerations can be made. The fact that curves T1 and T2 shift in temperature with frequency maintaining unvaried their shape implies that mostly the Debye function governs the relaxation through a fast law of $\tau(T)$, whilst the relaxation strength exhibits a relatively slow dependence. Otherwise, independently of frequency, one would expect a broad peak around the temperature $T = 0.65\,\frac{E}{k_B}$ where the relaxation strength function reaches the maximum. Thus, because the electrons and one phonon rate laws are slowly varying function of temperature while the two phonon (or multiphonon) rates are much more strongly dependent, we conclude that in the present processes the two phonon coupling is dominant.

Acknowledgements

One of the authors (O.F.) is grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support.

References

[1] J. Völkl, H. Wipf, B.J. Beaudry, K.A. Gschneider Jr., Phys. Status Solidi B 144 (1987) 315.
[2] I.S. Anderson, A. Heidemann, J.E. Bonnet, D.K. Ross, S.K.P. Wilson, M.W. McKergow, J. Less-Common Met. 101 (1984) 405.
[3] I.S. Anderson, D.K. Ross, J.E. Bonnet, Z. Phys. Chem. NF 164 (1989) S923.
[4] I.S. Anderson, N.F. Berk, J.J. Rush, T.J. Udovich, R.G. Barnes, A. Margel, D. Richter, Phys. Rev. Lett. 65 (1990) 1439.
[5] L. Lichty, R.J. Schoenberger, D.R. Torgeson, R.G. Barnes, J. Less-Common Met. 129 (1987) 31.
[6] R.G. Barnes, J.-W. Han, D.R. Torgeson, D.B. Baker, M.S. Conradi, R.E. Norberg, Phys. Rev. B 51 (1995) 3503.
[7] P. Vajda, J.N. Daou, P. Moser, P. Remy, Solid State Comm. 79 (1991) 383.
[8] P. Vajda, J.N. Daou, P. Moser, P. Remy, J. Phys.: Condens. Matter 2 (1990) 3885.
[9] G. Cannelli, R. Cantelli, F. Cordero, F. Trequattrini, I.S. Anderson, J.J. Rush, Phys. Rev. Lett. 67 (1991) 2682.
[10] R.G. Leisure, R.B. Schwarz, A. Migliori, D.R. Torgeson, I. Svare, I.S. Anderson, Phys. Rev. B 48 (1993) 887.
[11] R.G. Leisure, R.B. Schwarz, A. Migliori, D.R. Torgeson, I. Svare, Phys. Rev. B 48 (1993) 893.
[12] G. Cannelli, R. Cantelli, F. Cordero, F. Trequattrini, Phys. Rev. B 55 (1997) 14865.
[13] P. Vajda, Hydrogen in rare-earth metals, including RH_{2+x} phases, in: K.A. GschneidnerJr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 20, Elsevier Science B.V, 1995.
[14] L.R. Lichty, J.-W. Han, R. Ibanez-Meier, D.R. Torgeson, R.G. Barnes, E.F.W. Seymour, C.A. Sholl, Phys. Rev. B 39 (1989) 2012.
[15] I. Svare, D.R. Torgeson, F. Borsa, Phys. Rev. B 43 (1991) 7448.
[16] E. Fromm, E. Gebhardt (Eds.), Gäse und Kohlenstoff in Metallen, Springer, Berlin, 1976, pp. 363–364.
[17] I.S. Anderson, J.J. Rush, T. Udovic, J.M. Rowe, Phys. Rev. Lett. 57 (1988) 2822.
[18] T.D. Udovic, J.J. Rush, I.S. Anderson, R.G. Barnes, Phys. Rev. B 41 (1990) 3460.
[19] O. Blaschko, J. Pleschiutschnig, L. Pintschovious, A. Migliori, J.P. Burger, J.N. Daou, P. Vajda, Phys. Rev. B 40 (1989) 907.