PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Effect of Hydrogen on Superconductivity and Magnetism in high-T $_{\text{c}}$ Materials [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1995 **350**, 277-286
doi: 10.1098/rsta.1995.0014

The effect of hydrogen on superconductivity and magnetism in high-T_c materials

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The experimental results of measurements on hydrogen charged YBaCuO materials are critically reviewed and evaluated. The following subjects are discussed: (i) The site of hydrogen in $YBa_2Cu_3O_7$, (ii) superconductivity and normal state transport properties, (iii) structural changes and formation of a hydride phase and (iv) hydrogen-induced magnetism.

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1. Introduction

The interaction of hydrogen with high-T_c materials was studied by many groups in the past (see list of references, a more complete list of references can be found in Dortmann 1994) and a large amount of data is available. For some time, the experimental situation was rather confusing since unclear or even contradictory results were reported. In some papers the formation of water and the destruction of the material by hydrogen uptake was reported. Doubts came up whether hydrogen is at all incorporated in high-T_c materials or always just removes oxygen and forms water, thereby destroying the material.

The recent experiments, in particular those on thin films, clearly contradict this assumption. The observed structural changes upon hydrogen charging and the formation of a well defined hydrid phase are definitely not consistent with the destruction of the material. Also, the observation of a magnetic phase in $YBa_2Cu_3O_7$ in μSR experiments with a μSR frequency which is different from that of the O_6 material shows that hydrogen is incorporated into the intact material.

Conflicting data in the literature are probably due to differences in the charging conditions and the starting materials used. The charging temperature should not exceed 200–220 °C; the influence of the hydrogen pressure is not well known but lower pressures should be preferable. Concerning the materials, epitaxial films provide better defined conditions for the charging than powders or sintered samples. Since surfaces play an important role for the hydrogen uptake it is clear that the homogeneity of the hydrogen concentration is a serious problem in sintered samples and powders.

In this paper the available experimental data on this subject are critical reviewed and the present status of knowledge on hydrogen in high-T_c materials is summarized.

Phil. Trans. R. Soc. Lond. A (1995) **350**, 277–286
Printed in Great Britain

TEX Paper

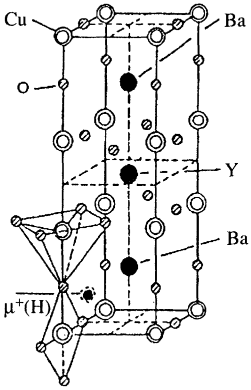


Figure 1. Tentative assignment of the hydrogen (muon) site in the $YBa_2Cu_3O_7$ unit cell. In Weber (1990) the position (0.15, 0.44, 0.071) in units of the lattice parameters is proposed as muon site.

2. The site of hydrogen in $YBa_2Cu_3O_7$

In metals, hydrogen usually occupies open interstitial sites or vacancies. Guided by this experience, the earlier literature on hydrogen in high-T_c materials (Fujii 1988; Niki 1989) assigned hydrogen to such sites also in $YBa_2Cu_3O_7$. However, this is probably not correct. There is now strong evidence from μSR studies but also from direct measurements on hydrogen that hydrogen (muon) is covalently bound to an oxygen atom in these materials.

The bonding idea was first propagated by Dawson (1988) and later taken up by many μSR researchers. A summary of the available μSR data on this subject is given in the article of Weber (1990). In this paper, the site assignment is based on a comparison of the local magnetic field measured at the muon site with fields calculated at different positions in the unit cell (see also Nishida 1990). Both, materials with magnetic ordering (e.g. $GdBa_2Cu_3O_{7-\delta}$ and hydrogen charged $H_xYBa_2Cu_3O_7$ or oxygen deficient $YBa_2Cu_3O_{6+\delta}$) as well as non-magnetic materials were taken into consideration. For non-magnetic materials the line width due to nuclear moments was calculated and compared with the experimental data. The authors come to the conclusion that the muon (and by analogy the hydrogen at low concentrations) is bound to oxygen in the Cu–O chain in $YBa_2Cu_3O_7$. The bond length is around 1 Å and the bond direction is approximately towards the apex oxygen. The suggested muon position is shown in figure 1.

This site assignment is only tentative since the magnetic field calculations are not rigorous (e.g. contact fields are neglected in the magnetic materials), but the consistency of the muon sites obtained in systems with very different magnetic structures strongly supports the assignment.

A completely independent information on the hydrogen site can be obtained from a study of the hydrogen vibrational modes. In an early infrared absorption study, an absorption at 1467 cm^{-1} was reported (Yang 1987) and assigned to a Cu–H vibration whereas the O–H vibration expected in the region around 3000–4000 cm^{-1} was not seen. The 1467 cm^{-1} absorption was not confirmed in a subsequent IR experiment (Richter 1992) nor in an inelastic neutron scattering study (Knell 1993) but a broad absorption at approximately 3400 cm^{-1} was recently observed in an IR experiment on hydrogen charged $YBa_2Cu_3O_7$ films

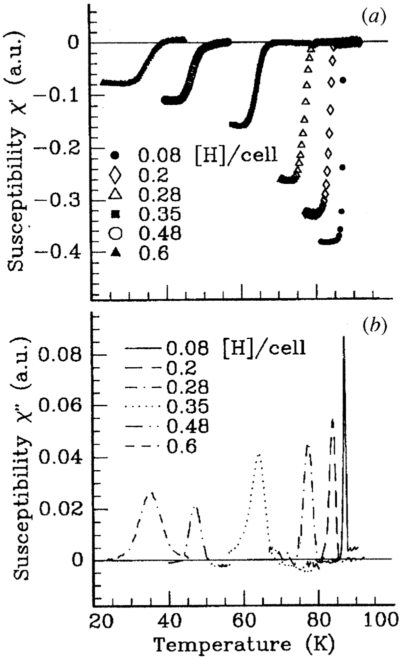


Figure 2. Real part χ' (shielding) and imaginary part χ'' (absorption) of the AC susceptibility as a function of the temperature and hydrogen concentration for $YBa_2Cu_3O_7$. The uncharged $YBa_2Cu_3O_7$ already contained an initial hydrogen concentration of [H] = 0.08 (Dortmann 1994).

(Erxmeyer 1991*a*). Thus, the present spectroscopy information suggest a strong O–H bonding and therefore supports the site assignment given above.

3. Superconductivity and the normal state properties

In Pd, the superconducting transition temperature can be increased by hydrogen charging (Stritzker 1972). In high-T_c materials there are also a few cases where an increase of T_c was observed by hydrogen charging (see, for example, Reilly 1987; Fujii 1988; Takabatake 1989) but these are all cases where T_c of the starting material was not optimum, i.e. the material was overdoped and by the introduction of hydrogen the optimum doping was generated. In general, hydrogen charging leads to a decrease of T_c.

Figure 2 shows the effect of hydrogen doping on the superconducting transition temperature of epitaxial $YBa_2Cu_3O_7$ films. In this figure the real (shielding, χ') and imaginary (absorption, χ'') part of the AC susceptibility is shown. Clearly, a shift of T_c towards lower temperatures with increasing hydrogen concentration is seen. This is in contradiction to the previous literature (Reilly 1987; Fujii 1988) where only a smearing out of T_c but no change of the onset temperature was reported. Since these earlier data are from sintered samples or powders which are less well defined than epitaxial films, it is plausible to assume that the intrinsic effect is a continuous shift of T_c as observed in the films and that the observation in bulk samples is due to inhomogeneities.

The onset temperature (intersection of straight lines through the susceptibility data above T_c and in the transition region) is shown in figure 3 as a function

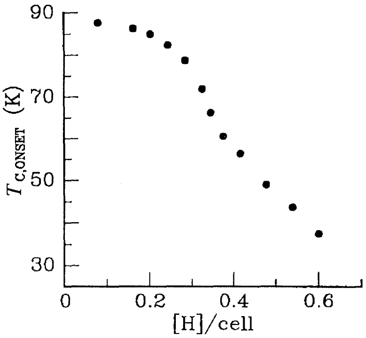


Figure 3. Relationship between $T_{c,onset}$ and the hydrogen concentration per unit cell for a $YBa_2Cu_3O_7$ film (Dortmann 1994).

of the hydrogen concentration. From Hall-effect measurements (Glückler 1991; Erxmeyer 1991*a*) we know that one hydrogen atom compensates approximately one unit of charge carrier, so that the abscissa in figure 3 gives approximately the reduction of charge carriers per unit cell. It can be seen from figure 3 that the initial charging reduces T_c only slightly whereas above $[H]/\text{cell} \approx 0.3$ a stronger reduction sets in. This is consistent with the observation that $YBa_2Cu_3O_7$ with the full O_7 stoichiometry is overdoped and a slight reduction of carriers, e.g. by oxygen removal, does not change T_c much.

An additional information from the Hall measurements (Dortmann 1994) is that the Hall mobility is not much influenced by hydrogen charging. Putting all this information together we come to the conclusion that hydrogen compensates charge carriers (consistent with the increase of the normal state resistivity (Dortmann 1994)) but does not introduce scattering centers for the charge carriers. The insensitivity of the mobility to hydrogen charging can be explained by assuming that the charge transport (in the CuO_2 plane) and the position of the hydrogen atom (in the CuO chain) are locally separated.

4. Structural changes and hydride phase

In the earlier experiments on bulk $YBa_2Cu_3O_7$ samples (Reilly 1987; Kamiyama 1987; Takabatake 1989), very weak changes of the lattice parameters were observed upon hydrogen charging at low hydrogen concentrations. At $[H]/\text{cell} \approx 0.8$, a transformation of the orthorhombic to tetragonal structure (see Fujii 1988) was observed, but since the orthorhombicity $(b-a)/a$, a and b being lattice parameters, is rather small this also involves only slight changes of the lattice constants. At higher concentrations usually a desintegration of the material or the formation of a hydride phase was assumed but the hydride phase was not observed in these studies.

Recently, in experiments on epitaxial $YBa_2Cu_3O_7$ thin films (Erxmeyer 1991*b*; Paulus 1992) a huge expansion of the *c*-axis lattice parameter upon hydrogen charging and the formation of a well defined hydride phase with $[H]/\text{cell} = 2$ was reported (see figure 4). The *c*-axis parameter of the hydride is 16% larger than that of the original material.

The developement of the X-ray diffraction pattern upon hydrogen charging can not be explained by a continuous expansion of the *c*-axis since this would

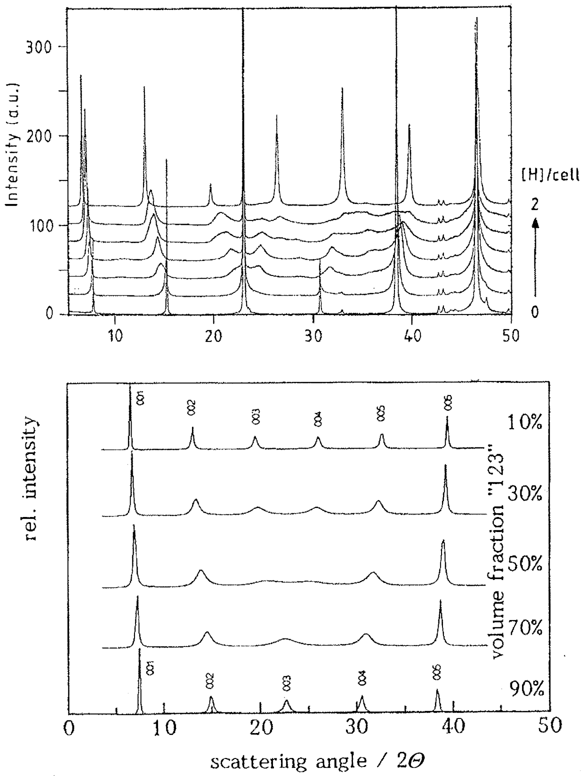


Figure 4. The developement of the X-ray diffraction reflections of a c-axis oriented $YBa_2Cu_3O_7$ film upon hydrogen uptake (Paulus 1992). Top: Experimental data. Bottom: Simulation assuming a statistical mixture of unexpanded ($c = 11.75$ Å) and fully expanded ($c = 13.65$ Å) layers. The fraction of unexpanded layers ("1 2 3") is varied from 90 to 10% and correspondingly the fraction of the expanded layers (hydride phase) from 10 to 90% (Paulus 1992).

lead to a continuous shift of the X-ray reflections lo lower angles contrary to the experiment where a much more complicated structure is seen at intermediate concentrations. Qualitatively, the behaviour can be reproduced (see figure 4) by assuming that the c-axis of the unit cell is either fully expanded, i.e. 16% larger, or not expanded at all and that the fraction of the two lattice parameters changes according to the hydrogen content. At the hydrogen concentration of $[H]/\mathrm{cell} = 2$ all layers are expanded and the whole sample has converted to the hydride phase. A proposal of the structure is shown in figure 5.

The earlier observations on bulk samples may be explained by assuming that the hydride phase was, due to the complexity of the X-ray pattern and due to inhomogeneous charging, missed and the observed pattern were due to the remaining fraction of the sample in the α-phase with a low hydrogen concentration. Recently, by concentrating on the low angle reflections, the hydride phase was also seen in bulk samples (Weidinger 1994).

5. Hydrogen induced magnetism

Hydrogen-induced magnetic ordering in $YBa_2Cu_3O_7$ was first observed in muon spin rotation (μSR) experiments (Niedermayer 1989). The appearance of a μSR

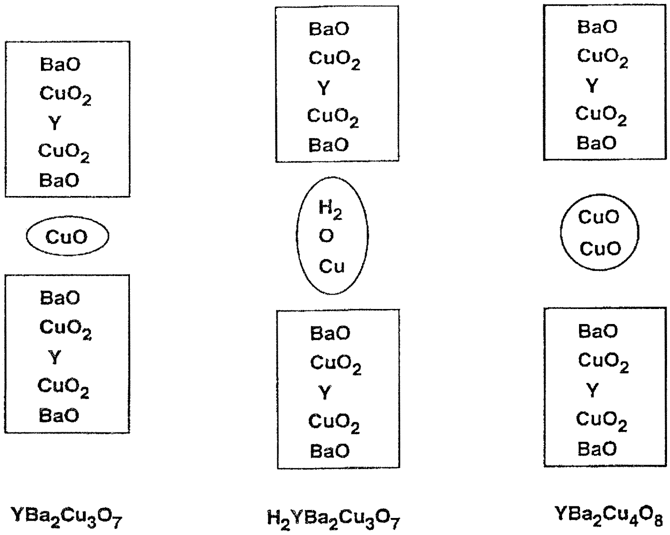


Figure 5. Proposed structure for the $H_2YBa_2Cu_3O_7$ hydride phase. It is suggested that the BaO–CuO_2–Y–CuO_2–BaO blocks remain basically unchanged and that the lattice expansion due to hydrogen uptake occurs in the CuO-chain area. On the left and right side, structure models of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ are displayed for comparison. The hydride phase has approximately the same c-axis as $YBa_2Cu_4O_8$, but the two structures are not identical.

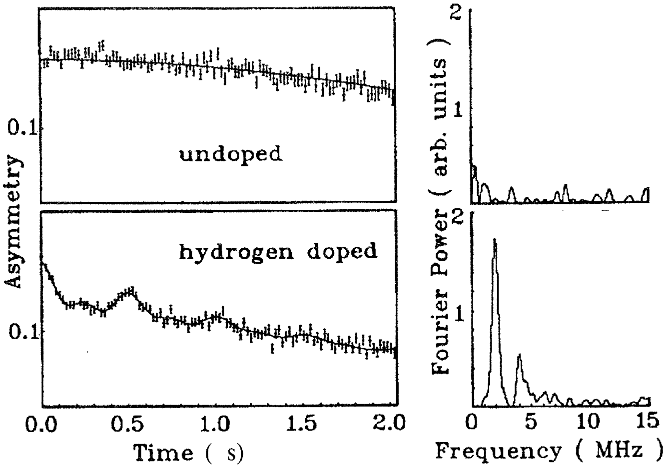
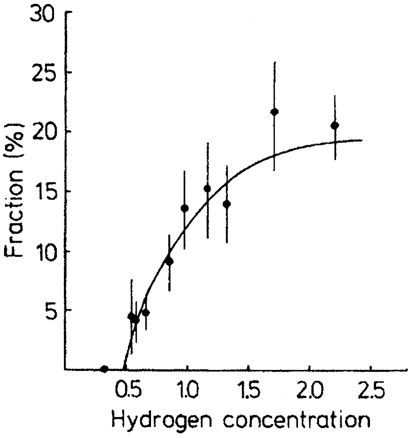


Figure 6. µSR spectra and their Fourier transforms for an uncharged and a hydrogen charged $YBa_2Cu_3O_7$ sample in zero external field. The oscillation in the lower spectrum is a clear indication of magnetic ordering in the sample (Niedermayer 1989).

precession in zero external field (see figure 6) is a clear indication of magnetic ordering. The authors found an onset of magnetic ordering at hydrogen concentrations between 0.5 and 1 and a saturation above approximately [H]/cell ≈ 1.5 (see figure 7). It is conceivable that the magnetic phase and the hydride phase are identical, although this is not proven yet.

The magnetic structure of H-charged $YBa_2Cu_3O_7$ is probably the same as that of oxygen deficient $YBa_2Cu_3O_{6+\delta}$, i.e. the Cu(II) moments order antiparallel in the CuO_2 plane. The calculated dipolar field for this magnetic structure at the



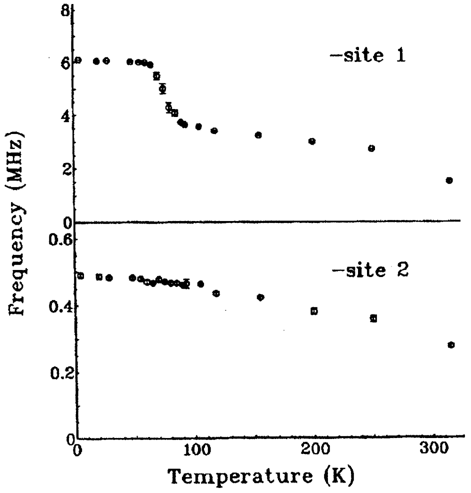


Figure 7. Fraction of muons which contribute to the 2 and 4 MHz signals as a function of the hydrogen concentration (Niedermayer 1989).

Figure 8. Temperature dependence of the observed μSR frequencies in hydrogen charged $YBa_2Cu_4O_8$ (Glückler 1993.) The two frequencies are assigned to two different bonding sites of the muon.

muon position given in §2 is consistent with the μSR frequency. If we assume that the magnetic phase is identical with the hydride phase this coincidence is accidental and we must assume that the muon occupies in the hydride structure a site where the magnetic field is the same as that calculated for the assumed muon position in the unhydrided sample. This is not unreasonable.

Recently, in an ^{1}H-NMR experiment (Gross 1992) the same internal magnetic field (150 G) was observed at the hydrogen site as observed with the muons. The internal field reported in an earlier publication (Goren 1989) is not consistent with this finding and actually was revoked in a later publication (Goren 1992).

Hydrogen induced magnetic ordering was observed also in $YBa_2Cu_4O_8$ (Glückler 1993). The remarkable jump in one of the μSR frequency (see figure 8) around 80 K is probably due to a site change of the muon. The authors speculate that this site change is connected to a slight structural reorientation of apex oxygen at this temperature. Up to now, hydrogen charging is the only way to drive the $YBa_2Cu_4O_8$ system into the magnetic phase.

6. Conclusion

The recent experiments clearly show that hydrogen is incorporated into the $YBa_2Cu_3O_7$ structure and that well defined phases (hydride and magnetically ordered) are formed. The possibility to create alternating superconducting and magnetic layers at intermediate (between 0 and 2) hydrogen concentrations is an attractive concept for further research.

References

Dawson, W. K., Dibbs, K., Weatherby, S. P., Boekema, C. & Chan, K.-H. 1988 Candidate muon-probe sites in oxide superconductors. *J. appl. Phys.* **64**, 5809–5811.

Dortmann, G., *et al.* 1994 Hydrogenation of thin YBaCuO films: electrical transport and structure properties of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$. *Phys. Rev.* B **49**, 600–606.

Erxmeyer, J. 1991*a* Herstellung dünner supraleitender $YBa_2Cu_3O_7$–Schichten und Untersuchung des Einflusses von Wasserstoff auf deren Eigenschaften. Ph.D. thesis, Freie Universität Berlin.

Erxmeyer, J., *et al.* 1991*b* Observation of a new phase in hydrogen-charged $YBa_2Cu_3O_7$ thin films. *Physica* C **185–189**, 1989–1990.

Fujii, H., Kawanaka, H., Ye, W., Orimo, S. & Fukuba, H. 1988 Effect of hydrogen absorption on superconductivity in $YBa_2Cu_3O_{6.91}$ and $GdBa_2Cu_3O_{6.89}$. *Jpn. J. appl. Phys.* **27**, L525–L528.

Glückler, H., *et al.* 1991 μSR and Hall-effect studies of the charge carrier concentration in hydrogenated $YBa_2Cu_3O_7$. *Europhys. Lett.* **15**, 355–360.

Glückler, H., Binninger, U., Niedermayer, Ch., Recknagel, E. & Weidinger, A. 1993 μSR studies of hydrogen induced magnetic ordering in high-T_c superconductor materials. *Z. Phys. Chemie* **179**, 389–395.

Goren, S. D., *et al.* 1989 Evidence of local magnetic order in the superconducting phase of hydrogen doped $YBa_2Cu_3O_7$ using nuclear magnetic resonance. *Solid State Comm.* **70**, 279–283.

Goren, S. D., *et al.* 1992 NMR of ^1H and ^2D in hydrogen doped and deuterium doped $YBa_2Cu_3O_7$. *Phys. Rev.* B**46**, 14142–14149.

Gross, J. & Mehring, M. 1992 Phase separation observed by ^{1}H-NMR in $YBa_2Cu_3O_{7-\delta}H_x$. *Physica* C **203**, 1–6.

Kamiyama, T., *et al.* 1987 Superconductivity in hydrogen-doped $YBa_2Cu_3O_{7-\delta}$. *Physica* B **148**, 491–493.

Knell, U., Wipf, H., Lauter, H. J. Udoviç & T. J. Rush 1993 A neutron spectroscopy study of the hydrogen vibrations in hydrogen-doped $YBa_2Cu_3O_x$. *J. Phys. Condensed Matter* **5**, 7607–7613.

Niedermayer, Ch., *et al.* 1989 Magnetic ordering induced by hydrogen doping of $YBa_2Cu_3O_7$. *Phys. Rev.* B**40**, 11386–11388.

Niki, H., *et al.* 1989 Proton NMR in hydrogen doped superconductor $YBa_2Cu_3O_{7-\delta}H_{0.2}$. *Solid State Comm.* **69**, 547–551.

Nishida, N. & Miyatake, H. 1990 Positive muon sites and possibility of anyons in the $YBa_2Cu_3O_7$ system. *Hyperfine Interact.* **63**, 189–195.

Paulus, W., *et al.*, 1992 Superconductor thin films: *in situ* X-ray study on the reaction of hydrogen with epitaxial $YBa_2Cu_3O_7$ layers. *Adv. Mater.* **4**, 416–419.

Reilly, J. J., Suenaga, M., Johnson, J. R., Thompson, P. & Moodenbaugh, A. R. 1987 Superconductivity in $H_xYBa_2Cu_3O_7$. *Phys. Rev.* B**36**, 5694–5697.

Richter, A., Irmer, G., Kessler, G., Panzer, M. & Herzog, K. 1992 Raman and IR spectroscopy of hydrogen-charged $YBa_2Cu_3O_{7-\delta}$ films. *J. Alloys Compounds* **187**, 59–66.

Stritzker, B. & Buckel, W. 1972 Superconductivity in Palladium–hydrogen and palladium–deuterium systems. *Z. Phys.* **257**, 1–8.

Takabatake, T., Ye, W., Orimo, S., Tamegai, T. & Fujii, H. 1989 Hydrogen intercalation in some superconducting copper oxids. *Physica* C **162–164**, 65–66.

Weber, M., *et al.* 1990 Identification of μ^+-sites in the 1-2-3 compound. *Hyperfine Interact.* **63**, 207–212.

Weidinger, A., *et al.* 1994 Magnetism in hydrogenated $YBa_2Cu_3O_7$: a comparison of μSR and NMR results. *Hyperfine Interact.* **86**, 609–614.

Yang, C. Y., *et al.* 1987 Superconducting $H_xYBa_2Cu_3O_7$: the role of H. *Phys. Rev.* B**36**, 8798–8802.

Discussion

W. JACKSON (*Palo Alto, CA, U.S.A.*). (1) Has Dr Weidinger performed neutron scattering on the YBCO hydride?

(2) Is the suppression of T_c due to a chemical reduction of the carrier density by the H or due to a lattice expansion which also is known to alter T_c?

A. WEIDINGER. (1) Several groups have performed neutron scattering experiments on hydrided and deuterided YBCO bulk samples but of course not on films. The Grenoble group (Fruchart *et al.* 1990) reports the observation of a new phase with $c = 1.53$ nm (note $c = 1.365$ nm in the present case) in heavily charged YBCO but they do not give the H-concentration of their sample. In our our neutron scattering experiment (unpublished) we observed diffraction diagrams which resembled in the low angle region those of figure 4 of the present paper at intermediate concentrations but in none of the experiments, even for [D]/cell = 2, was the new phase dominant. We did also not see the magnetic reflections expected for the magnetic phase. We assume that the corresponding lines are weak and broad and therefore can not be detected.

(2) The primary cause of the T_c reduction is in my opinion an electronic effect, but there is of course an intimate connection between the electronic structure and crystal structure and therefore there exists also a relation between T_c and the lattice parameters. Another question is whether proximity effects, i.e. the existence of non-superconducting regions near the superconducting areas are the cause of the T_c reduction. This is well possible.

G. LUKE (*Columbia University, U.S.A.*). What are the changes in the μ^+ site with oxygen doping from $YBa_2Cu_3O_6$–$YBa_2Cu_3O_7$?

A. WEIDINGER. If the chain oxygen is missing in oxygen deficient samples, the muon seems to bond to the apical oxygen. This site change is seen as a change of the intensities of the 2 MHz and 4 MHz lines which we assign to muons bound to chain oxygen and opical oxygen, respectively. The intensities correlate with the chain oxygen occupancy (see Glückler *et al.* 1989).

S. F. J. COX (*RAL, Oxfordshire, U.K.*). Does the way in which counterdoping by hydrogen suppresses T_c or induces magnetism shed any light on the mechanism of superconductivity?

A. WEIDINGER. The YBCO films at intermediate hydrogen concentrations (between [H]/cell = 0 and 2) constitute an interesting system. It seems that in these films, superconducting and magnetic layers are intermixed. We will continue the experiments on these films with classical methods but in the future also with very low energy muon beams. We think that such studies can shed light on the mechanism of superconductivity.

B. COLES (*Imperial College, London, U.K.*). Since Gd substituted YBCO has a RKKY coupled antiferromagnetism I think it unlikely that one can model the field due to a Gd moment as simply dipole in origin, which raises some uncertainty about the site of the muon.

A. SCHENCK (*ETH Zürich, Switzerland*). This is a comment concerning the question of a contact hyperfine field at the μ^+ in $YBa_2Cu_3O_7$: measurements in rare earth (Ho, Er, Dy) substituted compounds ($REBa_2Cu_3O_7$) did not reveal a rare earth induced μ^+ Knight shift (KS) (Weber 1991; Schenck *et al.* 1990), signalling essentially the absence of a local spin density at the μ^+. A high precision measurement of the μ^+-KS in $YBa_2Cu_3O_{7-\delta}$ yielded a small temperature independent value of + 24(7) p.p.m. and a temperature-dependent ($1/T$) contribution which was ascribed to a small fraction of paramagnetic Cu^{2+} ions present (Gygax *et al.* 1988). The small positive, temperature-independent contribution is probably of local origin and not induced by the CuO_2-planes. In contrast Mendels *et al.* (1994) claim to have found a sizeable contact hyperfine field at the μ^+ which is four times larger than the dipolar field originating from local moments in the CuO_2-planes. If this were the case also in the magnetically ordered phase no consistency in the site assignment of the μ^+ could have been reached from an analysis of all available spontaneous fields in the ordered phases of $YBa_2Cu_3O_{6+y}$, $H_xYBa_2Cu_3O_7$ and $REBa_2Cu_3O_7$ based on dipolar fields only (Weber *et al.* 1990). Nevertheless the issue remains interesting and more accurate measurements on high quality (monocrystalline) samples could be desirable.

M. SYMONS (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). I am puzzled by Doctor Weidinger's IR results for the O–H stretching mode (ν_{OH}). He sees a very broad band with a peak at *ca.* 3500 cm^{-1}. In my experience with solutions, this frequency corresponds to expectation for a non-hydrogen bonded X–OH hydrogen. When H-bonding occurs, as in X–OH$\cdots$B (where X is a covalently bonded unit, say, and B is any basic, lone-pair donor), the band maximum shifts to low frequencies (for strong H-bonds, this may move to below 3000 cm^{-1}), the band broadens, and the O–H oscillator strength increases. My question is, does Doctor Weidinger know why the band is so broad?

A. WEIDINGER. I suppose that the broadening is due to inequivalent surroundings of the O–H complex. Slight variations in the stoichiometry, or defects, might be the cause of this inequivalency.

M. SYMONS. If the source of the width is *via* coupling to neighbouring O–H oscillators, then can I suggest 'diluting' extensively with O–D units so that each O–H has O–D neighbours? The resulting O–H band should now be quite narrow, which would help you to detect different units, etc.

I want to avoid a possible nomenclature confusion, to which I fear I have contributed! By 'hydride', I think you mean such centres as the X–OH unit discussed above. I want to stress that this is, of course, totally different from units that contain anionic H^-, which is called the hydride ion. Thus, NaH is sodium hydride, but it in no way resembles the covalent species you refer to.

A. WEIDINGER. I accept that and will avoid the word 'hydride' for the YBCO-hydrogen phase in the future. We used the term in analogy to metal hydrides, where the term is used fairly loosely for all concentrated hydrogen–metal systems.

Additional references

Fruchart, D., *et al.* 1990 *J. Less-Common Metals* **157**, 233.
Glückler, H., *et al.* 1989 *Physica* C **162–164**, 149.
Gygax, F., *et al.* 1988 *Phys. Lett.* A **127**, 447.
Mendels, P., *et al.* 1994 *Phys. Rev.* B **49**, 10035.
Schenck, A., *et al.* 1990 *Hyperfine Interact.* **63**, 222.
Weber, H. 1991 Thesis, ETH Zürich.