Physica B 289–290 (2000) 567–569

PHYSICA B

www.elsevier.com/locate/physb

High-temperature trapping of muons in $CuInSe_2$ and $CuInS_2$

J.M. Gil[a,*], H.V. Alberto[a], R.C. Vilão[a], J. Piroto Duarte[a], P.J. Mendes[a], N. Ayres de Campos[a], A. Weidinger[b], Ch. Niedermayer[c], M.V. Yakushev[d], R.D. Pilkington[d], R.D. Tomlinson[d], S.F.J. Cox[e,f]

[a] *Physics Department, University of Coimbra, P-3000 Coimbra, Portugal*
[b] *Hahn-Meitner Institut Berlin, Glienicker Str. 100, D-14109 Berlin, Germany*
[c] *Faculty of Physics, University of Konstanz, D-78434 Konstanz, Germany*
[d] *Physics Department, University of Salford, Salford M5 4WT, UK*
[e] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK*
[f] *Physics Department, University College London, London WC1E 6BT, UK*

Abstract

Zero-field μSR measurements were performed at the EMU muon beamline of the ISIS facility on single crystals of p- and n-type $CuInSe_2$ and on crystallites of p-type $CuInS_2$.The diamagnetic centre, thought to be located in all these compounds at the Se anti-bonding interstitial site at low temperatures, is seen to diffuse above 200 K in the Se compound and above 250 K in the S compound. At 380 K the muons are again motionless in $CuInSe_2$. This is evidence that the muons are trapped at defects. The fitted low values of the static dipolar width at the trapping sites are consistent with a static muon in a vacancy. This interpretation implies a vacancy concentration in the order of $10^{20}\,cm^{-3}$, unless the trapping radius is particularly large. However, defects other than vacancies may be involved. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chalcopyrites; Hydrogen-like defects; Muon trapping; μSR

1. Introduction

Chalcopyrites like $CuInSe_2$ and $CuInS_2$, and derivatives obtained by partial replacement of In by Ga, have been introduced in the manufacturing of solar cells exhibiting large energy conversion efficiencies. Hydrogen is known to interact strongly with dopants and intrinsic defects in semiconductors, which makes it a useful tool in controlling the performance of devices. Its effects on chalcopyrites have been a subject of increasing research [1–3].

Extensive experimental and theoretical studies of defects in chalcopyrites [4,5] indicate that these are highly doped and highly compensated materials. The concentration of specific species of defects depend on the deviation from stoichiometry in the compound, and numbers as large as $10^{18}\,cm^{-3}$ have been reported for, e.g., Cu vacancies (V_{cu}) [6].

The particularity of μSR techniques in the study of isolated hydrogen (of which muonium is considered a light isotope) in semiconductors has been

* Corresponding author. Fax: + 351-239-829158.
E-mail address: fnoa@ci.uc.pt (J.M. Gil).

PII: S0921-4526(00)00258-1

applied very successfully in the study of elemental Group-IV (Si, Ge) and III–V compound semiconductors (e.g. GaAs) [7–9]. Recently, the same techniques started to be applied to II–VI compounds and chalcopyrites [10,11].

In the first study of $CuInSe_2$ and $CuInS_2$ [11], we reported the location of the diamagnetic centre, thought to be located in these compounds at the Se anti-bonding interstitial site (AB site) at low temperatures, and the observation of its diffusion above 200 K in the Se compound and above 250 K in the S compound. No muonium was observed, but at low temperatures a missing fraction of 6–10% was noticed. In the present work, those studies were extended to higher temperatures, where the presence of trapping was already suggested in the earlier results at around room temperature.

2. Experimental details

The samples used in the present work were the same as in the earlier low temperature (10 K to room temperature) study.

The $CuInSe_2$ samples were single crystals produced by the vertical Bridgman technique. One p- and one n-type crystal were used. The elemental composition of the p-type crystal, as determined by Rutherford back-scattering (RBS) and energy dispersive X-ray analysis (EDX), was Cu (25.52 at%), In (25.33 at%), Se (49.14 at%), and the total carrier concentration at room temperature was of the order of $5 \times 10^{16}\,cm^{-3}$. The elemental composition of the n-type crystal was determined by EDX to be Cu (26.47 at%), In (23.63 at%), Se (49.90 at%), and the total carrier concentration at room temperature was of the order of $1 \times 10^{16}\,cm^{-3}$.

The $CuInS_2$ sample consisted of crystallites prepared by chemical-vapour deposition under a temperature gradient. The material obtained was p-type with a total carrier concentration in the order of typically $10^{14}\,cm^{-3}$.

Zero-field (ZF) measurements were performed at the EMU muon beamline of the ISIS Facility (Rutherford Appleton Laboratory, Oxfordshire, UK) in the temperature range from room temperature up to 500 K.

3. Results and discussion

The zero-field data below room temperature were presented in Ref. [11]: in that analysis, a single dynamic Kubo–Toyabe (K–T) function [12] was fitted to the data, fixing the low-temperature value of the dipolar width. A jump rate for Mu^+ diffusion among AB sites could be measured above 200 K in the Se compound and above 250 K in the S compound. Such a fit was not giving good results above 250 K (Se compound), nor above 300 K (S compound).

In the present work we present a preliminary analysis of the same low-temperature data as well as the new high-temperature spectra fitted with a static K–T function, the dipolar width presented in Fig. 1 for all the studied samples parameterizing the dipolar interaction with the Cu and In nuclei of the lattice. Diffusion is in this analysis evident as a decrease in the dipolar width, a motional narrowing in the time spectra.

If the muons would just be subjected to a long-range diffusion, the motional narrowing would drive the dipolar width to zero at an appropriate value of temperature. The peak found in $CuInSe_2$ around 380 K is an indication of trapping, as is also found in the cases of GaAs and InP [13,14]. At this temperature and for this compound a single static K–T function gives a good fit, with a dipolar width

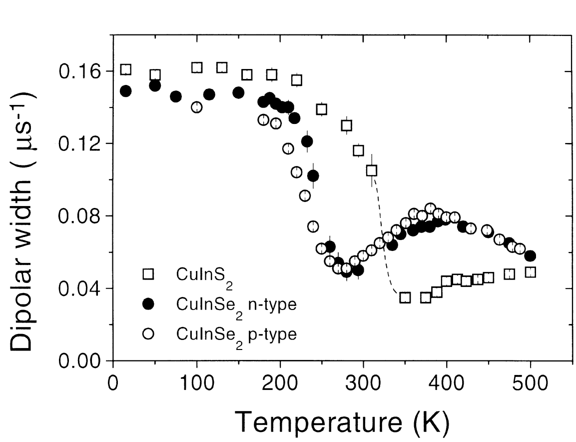

Fig. 1. Temperature dependence of the zero-field dipolar width, measured on p- and n-type $CuInSe_2$ single crystals and on $CuInS_2$ crystallites. The values were obtained from fits of a static Kubo–Toyabe function.

of around 0.08 μs^{-1}, which is strongly indicative of the muons being stopped at trapping sites at this temperature. Above and below the peak, and at all temperatures above 300 K in the S compound, the data are not well fitted with either one or two static or dynamic K–T functions. Detrapping is possibly occurring above 380 K in the Se compound, while in the S compound the complete trapping and detrapping process is possibly occurring within the timewindow of 16 μs. As a consequence, the dipolar width obtained from a fit of a static K–T function is lower than expected for a static muon at the same trapping site.

A static KT function implies that the muon is trapped within a time in the order of 1 μs, but this time requires further confirmation. Extrapolating our earlier results [11], the jump rate at 380 K would be about 40 μs^{-1}. In a purely statistical model, the muons would visit about 40 sites in a microsecond and would be trapped if they get within the trap radius of a trap site. If we assume that trapping occurs when the muon reaches an antibonding site of a nominally Cu–Se bond in the vicinity of a vacancy, then the vacancy concentration would have to be in the order of 10^{20} cm^{-3}.

Although the dipolar width found in $CuInSe_2$ at 380 K is consistent with the muons being stopped in a vacancy, where the distances to the Cu and In dipolar nuclei are larger than for the normal interstitial sites, the number of vacancies is probably smaller than 10^{20} cm^{-3}. One possible interpretation is that the trapping radius of the vacancy is rather large and therefore enhances the trapping probability over a purely statistical probability. However, defects other than a vacancy are not ruled out as the trapping centre, if we consider the possibility of the dipolar width not reflecting the static value, but a lower value being measured. The application of a two-state trapping–detrapping model [15] will clarify further these points.

Acknowledgements

The help of the μSR Group at ISIS for supporting experiments is gratefully acknowledged. This work was partially supported by PRAXIS XXI (Portugal, PCEX/P/FIS/16/96), EPSRC (UK, GR/L 62757), and EU TMR program for Large-Scale Facilities (research at ISIS).

References

[1] M.V. Yakushev, R.W. Martin, G. Lippold, H.W. Schock, J.A. Van den Berg, D.G. Armour, R.D. Pilkington, A.E. Hill, R.D. Tomlinson, Proceedings of the 14th European Photovoltaic Solar Energy Conference, Barcelona, 1997, p. 2147.

[2] D. Fink, J. Krauser, G. Lippold, M.V. Yakushev, R.D. Tomlinson, A. Weidinger, K.K. Dwivedi, S. Ghosh, W.H. Chung, Rad. Eff. Def. Sol. 145 (1998) 85.

[3] A. Weidinger, J. Krauser, Th. Riedle, R. Klenk, M.Ch. Lux-Steiner, M.V. Yakushev, Mat. Res. Soc. Symp. Proc. 513 (1998) 177.

[4] S.B. Zhang, Su-Huai Wei, A. Zunger, H. Katayama-Yoshida, Phys. Rev. B 57 (1998) 9642.

[5] J. Krustok, H. Collan, M. Yakushev, K. Hjelt, Phys. Scripta T79 (1999) 179.

[6] J. Klais, H.J. Möller, D. Cahen, Proceedings of the E-MRS, Strasbourg, June 1999,. O–820.

[7] B. Hitti, S.R. Kreitzman, T.L. Estle, E.S. Bates, M.R. Dawdy, T.L. Head, R.L. Lichti, Phys. Rev. B 59 (1999) 4918.

[8] R.L. Lichti, S.F.J. Cox, K.H. Chow, E.A. Davis, T.L. Estle, B. Hitti, E. Mytilineou, C. Schwab, Phys. Rev. B 60 (1999) 1734.

[9] S.F.J. Cox, R.L. Lichti, J. Alloys Compounds. 253–254 (1997) 414.

[10] J.M. Gil, H.V. Alberto, R.C. Vilão, J. Piroto Duarte, P.J. Mendes, N. Ayres de Campos, A. Weidinger, J. Krauser, Ch. Niedermayer, S.F.J. Cox, Physica B 289–290 (2000), these proceedings.

[11] J.M. Gil, P.J. Mendes, L.P. Ferreira, H.V. Alberto, R.C. Vilão, N. Ayres de Campos, A. Weidinger, Y. Tomm, Ch. Niedermayer, M.V. Yakushev, R.D. Tomlinson, S.P. Cottrell, Phys. Rev. B 59 (1999) 1912.

[12] R.S. Hayano, Y.J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, R. Kubo, Phys. Rev. B 20 (1979) 850.

[13] K.H. Chow, Hyperfine Interactions 105 (1997) 285.

[14] R.L. Lichti, S.F.J. Cox, C. Schwab, T.L. Estle, B. Hitti, K.H. Chow, Hyperfine Interactions 105 (1997) 333.

[15] M. Borghini, T.O. Niinikoski, J.C. Soulié, O. Hartmann, E. Karlsson, L.O. Norlin, K. Pernestål, K.W. Kehr, D. Richter, E. Walker, Phys. Rev. Lett. 40 (1978) 1723.