Investigation of the magnetic hyperfine field at the Y site in the Heusler alloys $Co_2Y^1_{1-x}Y^2_xZ$ (Y = Ti,V,Nb,Cr; Z = Al,Sn)

Investigation of the magnetic hyperfine field at the Y site in the Heusler alloys $Co_2Y^1_{1-x}Y^2_xZ$ (Y = Ti, V, Nb, Cr; Z = Al, Sn)

W Pendl Jr†§, R N Saxena†, A W Carbonari†, J Mestnik Filho† and J Schaff‡

† Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil
‡ Instituto de Fisica, UFRGS, Porto Alegre, Brazil

Abstract. The magnetic hyperfine field (mhf) acting on a ^{181}Ta probe dilutely substituted at the non-magnetic transition element site has been investigated for the pseudo-quaternary Heusler alloys $Co_2Ti_{1-x}Nb_xAl$, $Co_2Ti_{1-x}V_xAl$, $Co_2Ti_{1-x}V_xSn$, and $Co_2V_{1-x}Cr_xAl$ with $x = 0.2, 0.4, 0.6$ and 0.8 by TDPAC measurements utilizing the 133–482 keV gamma–gamma cascade in ^{181}Ta following the β^--decay of ^{181}Hf. Magnetization measurements on $Co_2Ti_{1-x}(Nb, V)_xAl$ samples were carried out by using a vibrating-sample magnetometer. The Curie temperature and the saturation magnetization were obtained for each alloy. The lattice parameters of the alloys were determined by x-ray diffraction measurements. The results for the mhf acting on Ta occupying the non-magnetic transition element site are discussed and compared with the mhf systematics for the cobalt-based Heusler alloys.

1. Introduction

The Heusler alloys are ternary intermetallic compounds which exhibit a magnetic order and, since the atoms occupy well defined positions in a cubic structure in these compounds, they provide an excellent environment where a systematic behaviour of the magnetic hyperfine field can be studied by varying the constituent elements of the alloy. The $L2_1$ Heusler alloys have stoichiometric composition X_2YZ, where: X is usually a transition or noble metal such as Cu, Pd, Ni; Y is a transition element such as Ti, Zr, Hf, V, Nb; and Z is an sp element belonging to group IIIA to VA. The Co-based Heusler alloys Co_2YZ are of particular interest because the local magnetic moments, carried by the Co atoms in these alloys, are known to have values ranging from 0.3 to 1.0 μ_B, in contrast to the alloys of the form X_2MnZ, with X $\neq$ Co, where the magnetic moment of about 4 μ_B is localized on the Mn atoms. This fact is most probably related to the number of localized or itinerant d electrons in each type of alloy which contribute to the local magnetic moment. Furthermore, in the Heusler alloys Co_2YZ the nearest-neighbour Co–Co distance is only slightly larger than in pure Co and it is quite possible that direct exchange interactions play an important role in determining their magnetic properties. Long-range magnetic coupling of localized moments via conduction electrons is however widely accepted as the dominant exchange mechanism in Heusler alloys.

§ Present address: Universidade Cidade de São Paulo (UNICID), Departamento de Ciências Exatas, São Paulo, Brazil.

In previous work [1–3] some interesting features of the hyperfine fields at non-magnetic atoms in the cobalt-based alloys have been reported. The reduced mhf either at the non-magnetic transition element site or at the sp element Sn in the Co_2YZ Heusler alloy has been shown to depend mainly on the chemical nature of the non-magnetic transition element at the Y-atom site. Another important observation is that the reduced mhf at the Sn as well as at the non-magnetic transition element site follows the generally observed trend where the field increases with increasing conduction electron density. The reduced field increases for example when a group IIIB element Sc at a Y site is substituted for with a group IVB element Ti, Zr, or Hf with a higher number of d electrons (see figure 1). The behaviour of V, Nb, Ta and Cr is however anomalous in this respect since the reduced field *decreases* when a group IVB element is replaced by a group VB element or a group VIB element with a still higher number of d electrons. The systematics of the Co-based Heusler alloys has been discussed by Carbonari *et al* [3] in terms of the Blandin and Campbell (BC) model to explain this anomalous behaviour.
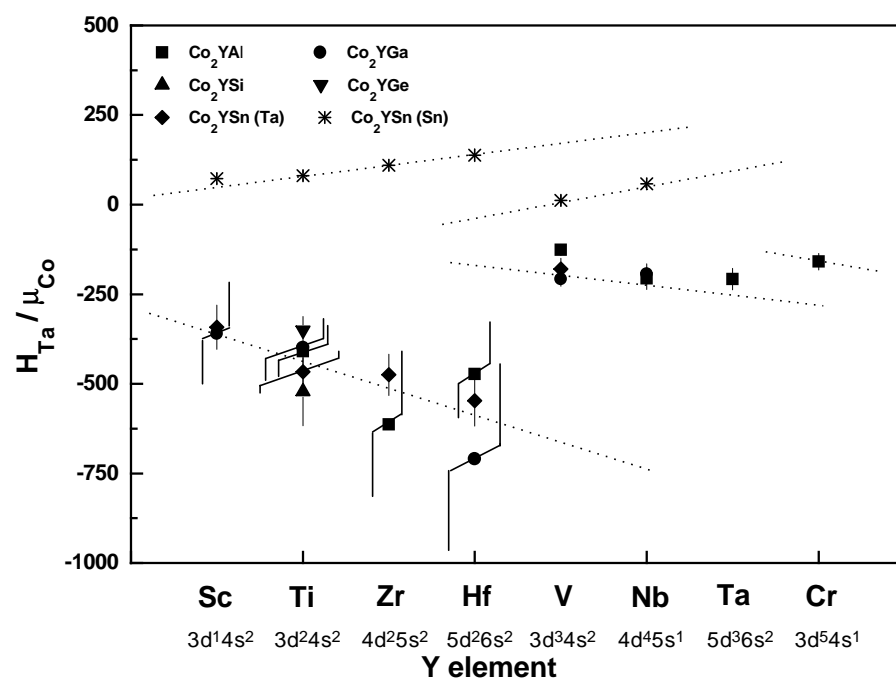

Figure 1. The reduced mhf at Ta and Sn as a function of the outer-electron configuration of the Y-site transition element in the Co_2YZ Heusler alloys.

In order to further investigate this behaviour as well as to study the Y-site hyperfine field as a function of the chemical nature of the transition element, especially when it is switched from a group IVB element to a group VB or group VIB element, we have carried out time-differential perturbed angular correlation (TDPAC) measurements of the mhf acting on ^{181}Ta at the Y sites in the pseudo-quaternary Heusler alloys $Co_2Ti_{1-x}Nb_xAl$, $Co_2Ti_{1-x}V_xAl$, $Co_2Ti_{1-x}V_xSn$ and $Co_2V_{1-x}Cr_xAl$ with $x = 0.2, 0.4, 0.6$ and 0.8. The hyperfine-field results are discussed and compared with the observed systematics in other Co-based Heusler alloys.

2. Experimental details

The TDPAC method is based on hyperfine interaction of nuclear moments with external magnetic fields or electric field gradients. A detailed description of the TDPAC method can be found in reference [4]. In the present work we are concerned only with the magnetic field, since the electric field gradient tensor should vanish due to the cubic symmetry of the charge distribution around a particular atomic site in the Heusler alloys.

The interaction between the magnetic dipole moment of the nucleus μ and the magnetic hyperfine field H is given by the Hamiltonian $H = -\mu \cdot H$. The eigenvalues E_m are given by $E_m = -g\mu_n H m$, where g is the nuclear g-factor and μ_n is the nuclear magneton, producing the energetically equidistant Zeeman splitting. The energy difference between two adjacent sub-levels is

$$\Delta E = E_{m+1} - E_m = \hbar\omega = g\mu_n H. \tag{1}$$

The TDPAC method uses a radioactive nuclear probe which decays via a $\gamma-\gamma$ cascade through an intermediate energy level with spin I which, in the presence of an external magnetic field, precesses with a Larmor frequency ω_L given by $\omega_L = g\mu_n H/\hbar$.

The ^{181}Hf used as the nuclear radioactive probe in the present study decays with a half-life of 42 days via β^--emission mainly to the 615 keV excited state of the ^{181}Ta which in turn decays via a 133–482 keV $\gamma-\gamma$ cascade to the ground state. The intermediate level is characterized by $I = 5/2$ and a half-life of 10.8 ns.

The perturbed time-differential $\gamma-\gamma$ angular correlation in polycrystalline samples is expressed (neglecting the A_{44}-terms) by the following function:

$$W(\theta, t) = 1 + A_{22} G_{22}(t) P_2(\cos\theta) \tag{2}$$

where θ is the angle between the detectors, A_{22} is the unperturbed angular correlation coefficient of the $\gamma-\gamma$ cascade, $P_2(\cos\theta)$ is the Legendre polynomial and $G_{22}(t)$ is the perturbation factor. For an unpolarized ferromagnetic sample consisting of randomly oriented domains this factor can be written as

$$A_{22} G_{22}(t) = A_{22}[0.2 + 0.4\cos\omega_L t + 0.4\cos 2\omega_L t] \tag{3}$$

where $\omega_L = \mu_n g H_{hf}/\hbar$ is the Larmor frequency. The g-factor of the 482 keV $(5/2)^+$ state of ^{181}Ta is known to be $g_{5/2} = 1.3(1)$ [5]. It is thus possible to determine the ^{181}Ta hyperfine field H_{hf} from the measured Larmor frequency.

The Heusler alloy samples were prepared by arc melting the constituent elements (purity better than 99.9%) under an argon atmosphere along with the radioactive ^{181}Hf substituting for approximately 0.1% of the atoms of the Y-site transition element in each case. The resulting alloys were homogenized at 900 °C for 24 h and cooled slowly. The samples were then crushed and annealed at 800 °C for 24 to 72 h in an argon atmosphere and quenched into water. All of the samples were analysed by x-ray diffraction to ensure that they had the correct $L2_1$ structure. The x-ray measurements were made with a powder diffractometer using Cu Kα radiation.

The TDPAC measurements were carried out with a conventional fast–slow coincidence set-up using BaF$_2$ detectors having a time resolution of about 0.9 ns. The measurements of $A_{22}G_{22}(t)$ were performed at 77 K in all cases. Another run of measurement was made above the Curie temperature to verify that the alloy was in fact of cubic structure and showed no quadrupole interaction. The sign of the field was measured by the usual method using an externally applied magnetic field of the order of 0.5 T.

The saturation magnetization measurements for the alloys Co$_2$Ti$_{1-x}$Nb$_x$Al and Co$_2$Ti$_{1-x}$V$_x$Al were made in a conventional Foner-type vibrating-sample magnetometer.

The measurements were made in the temperature range of 5 to 500 K in an applied field of 0.2 T at which the magnetization was found to be saturated. The system was calibrated with a pure (99.999%) Ni foil.

Table 1. Magnetic and structural properties of the Heusler alloys studied.

Alloy	a (Å)	T_C (K)	μ_{Co} (μ_B)	H_{Ta} (0 K) (kOe)	H_{Ta}/μ_{Co} (kOe/μ_B)
Co_2TiAl	5.85[a]	148[b]	0.37[a]	−168(5)[b]	−454(15)
$Co_2Ti_{0.8}Nb_{0.2}Al$	5.87	253	0.56(2)	−259(4)	−464(18)
$Co_2Ti_{0.6}Nb_{0.4}Al$	5.87	262	0.55(2)	−271(6)	−493(21)
$Co_2Ti_{0.4}Nb_{0.6}Al$	5.89	290	0.77(2)	−311(12)	−404(19)
$Co_2Ti_{0.2}Nb_{0.8}Al$	5.94	327	0.94(2)	−416(14)	−442(9)
Co_2NbAl	5.94[c]	383[a]	0.67[a]	−141(5)[c]	−210(7)
$Co_2Ti_{0.8}V_{0.2}Al$	5.82	207	0.51(2)	−257(6)	−502(23)
$Co_2Ti_{0.6}V_{0.4}Al$	5.75	247	0.50(2)	−275(10)	−549(30)
$Co_2Ti_{0.4}V_{0.6}Al$	5.79	288	0.68(2)	−285(9)	−420(18)
$Co_2Ti_{0.2}V_{0.8}Al$	5.78	313	0.97(2)	−352(11)	−364(14)
Co_2VAl	5.77[a]	310[a]	0.92[a]	−121(5)[c]	−131(5)
$Co_2V_{0.8}Cr_{0.2}Al$	5.75	315[d]	0.81[d]	−110(7)	−135(9)
$Co_2V_{0.6}Cr_{0.4}Al$	5.75	335[d]	0.90[d]	−145(4)	−161(4)
$Co_2V_{0.4}Cr_{0.6}Al$	5.75	345[d]	0.95[d]	−160(3)	−169(3)
$Co_2V_{0.2}Cr_{0.8}Al$	5.73	320[d]	0.90[d]	−203(9)	−225(10)
Co_2CrAl	5.73[d]	334[a]	0.78[a]	−131(5)[e]	−167(6)
Co_2TiSn	6.08[f]	371[f]	0.98[f]	−494(12)	−504(13)
$Co_2Ti_{0.8}V_{0.2}Sn$	6.03	—	0.98(5)[g]	−286(5)	−292(16)
$Co_2Ti_{0.6}V_{0.4}Sn$	6.01	—	1.07(5)[g]	−304(8)	−284(15)
$Co_2Ti_{0.4}V_{0.6}Sn$	5.99	—	0.91(5)[g]	−313(15)	−344(25)
$Co_2Ti_{0.2}V_{0.8}Sn$	5.96	—	0.88(5)[g]	−430(12)	−490(31)
Co_2VSn	5.98[c]	95[f]	0.60[f]	−216(5)[c]	−360(8)

[a] Reference [8].
[b] Reference [1].
[c] Reference [2].
[d] Reference [7].
[e] Reference [3].
[f] Reference [9].
[g] Reference [6].

3. Results and discussion

The local magnetic moment (μ_{Co}) as well as the Curie temperature (T_c) obtained from the magnetization measurements and the lattice parameter (a) determined from x-ray diffraction data are presented in table 1 together with additional results from previous work [6–9]. The magnetization curves for $Co_2Ti_{1-x}V_xAl$ alloys are shown in figure 2.

Typical examples of the TDPAC spectra for some of the alloys are shown in figure 3. Solid curves represent the least-squares fit of the experimental data to expression (3). Results of the fitting indicated that most of the alloys had unique fields with small distributions. However, the alloys $Co_2Ti_{0.2}Nb_{0.8}Al$, $Co_2Ti_{0.2}V_{0.8}Sn$, $Co_2Ti_{0.6}V_{0.4}Sn$ and $Co_2V_{0.2}Cr_{0.8}Al$ showed two distinct fields with approximately 30% of the Ta nuclei probing a somewhat
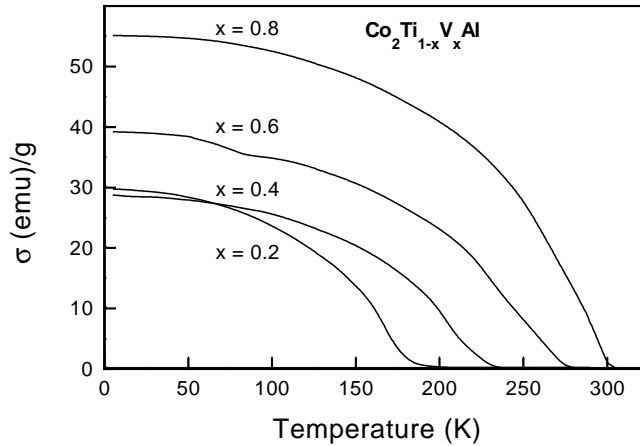
Figure 2. Temperature dependences of the magnetization observed in $Co_2Ti_{1-x}V_xAl$ alloys in the applied field of 0.2 T.

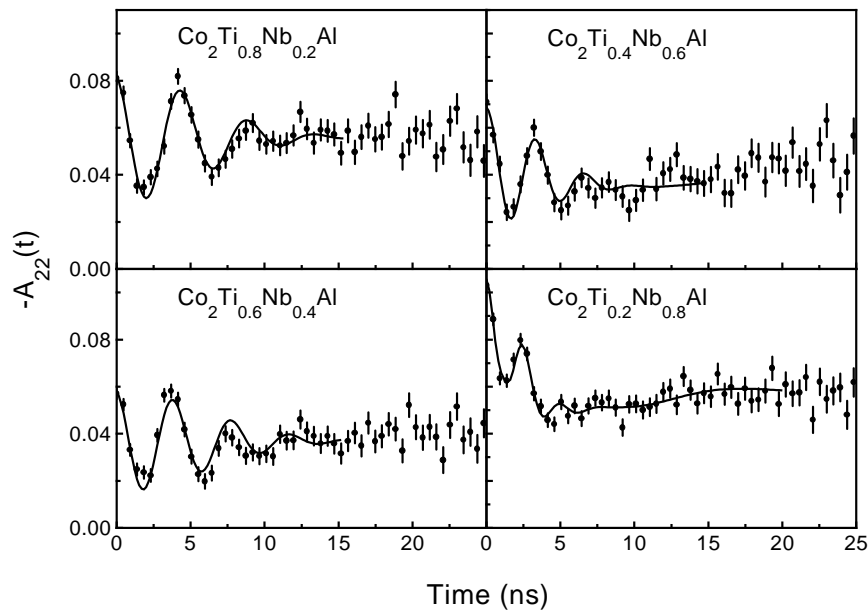**Figure 3.** TDPAC spectra obtained for the alloys $Co_2Ti_{1-x}Nb_xAl$ at 77 K.

smaller field. Since the x-ray results did not reveal the presence of a second phase we attribute this to Ta nuclei occupying other sites within the $L2_1$ structure. The magnetic hyperfine fields H_{Ta} for the Heusler alloys determined in the present study are given in table 1. The fields given in this table are the values extrapolated to 0 K. Additional results for the ternary alloys taken from previous work [1–3] have been included in this table.

The mhf acting on Ta at the Y site extrapolated to 0 K is plotted in figure 4 as a function of the concentration of the element Y^2 in the alloys $Co_2Y^1_{1-x}Y^2_xZ$. The experimental data points in each series of alloys have been joined by straight lines just to guide the eye.
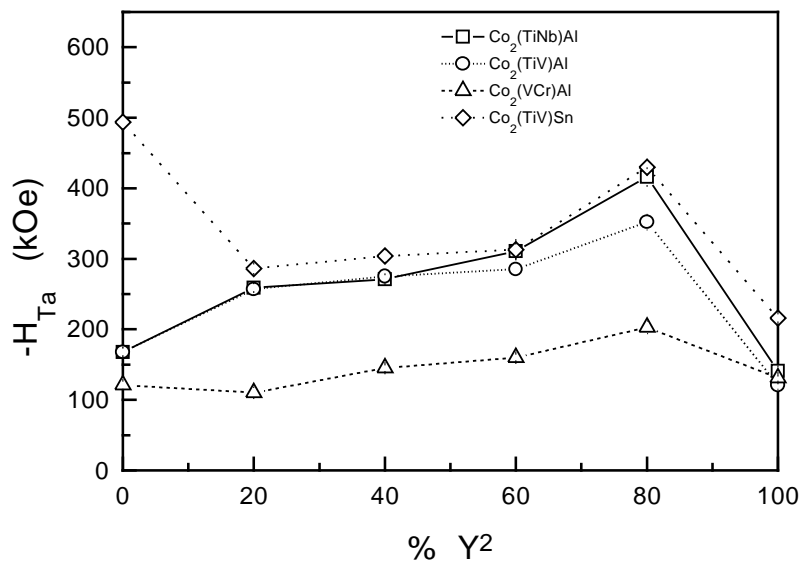
Figure 4. The magnetic hyperfine field at Ta as a function of the Y^2-element fraction in the alloys $Co_2Ti_{1-x}(V, Nb)_xAl$, $Co_2V_{1-x}Cr_xAl$ and $Co_2Ti_{1-x}V_xSn$.

The results show that the Ta fields in the alloys $Co_2Ti_{1-x}V_xAl$ and $Co_2Ti_{1-x}Nb_xAl$ exhibit almost identical behaviours. The field increases gradually although not quite linearly in the range $0.0 \leqslant x \leqslant 0.8$ and then drops suddenly at $x = 1.0$. The behaviour of the field in the alloys $Co_2V_{1-x}Cr_xAl$ is broadly similar to that in the $Co_2Ti_{1-x}V_x(Nb_x)Al$ alloys, although less dramatic in showing a maximum at around $x = 0.80$. Except for a sudden drop from about -500 kOe at $x = 0.0$ to about -290 kOe at $x = 0.2$ the hyperfine field for the alloys $Co_2Ti_{1-x}V_xSn$ also follows a similar trend to that for the alloys $Co_2Ti_{1-x}(V, Nb)_xAl$.

The local magnetic moments on Co for the alloys $Co_2Ti_{1-x}(V, Nb)_xAl$ were determined from the saturation magnetization data and the results are presented in table 1 together with the previous results for the alloys $Co_2Ti_{1-x}V_xSn$ taken from reference [6] and for the alloys $Co_2V_{1-x}Cr_xAl$ taken from reference [7]. We have chosen to include the values of 0.60 μ_B for μ_{Co} in the alloy Co_2VSn and 0.98 μ_B in Co_2TiSn from reference [9] instead of the values given in reference [6], because they are the results of a more recent measurement and also because the values provide a better agreement with the observed systematics of the reduced fields in Co_2YZ alloys [2, 3]. Figure 5 shows the plot of the local magnetic moment as a function of the concentration of the Y^2 element in the alloys studied. Once again the experimental data points in each family of alloys are joined by straight lines for better visualization. It must be pointed out at this point that the saturation magnetization measurements alone cannot provide information on the distribution of the total moment at different atomic sites. A large number of cobalt-based Heusler alloys including the alloys Co_2YZ ($Y = Ti$, V, Nb; $Z = Al$, Sn) have however been studied in the past [10, 11] by neutron diffraction where it was established that the entire magnetic moment is localized on the Co atom. There are no reports on neutron diffraction study of the alloy Co_2CrAl. Saturation magnetization measurements in conjunction with the spin-echo NMR measurements on Co_2CrAl [7] however indicated the possibility of having some magnetic moment localized on Cr atoms although no quantitative estimates were made. In the discussion of the present results we will however assume that only the cobalt atom has
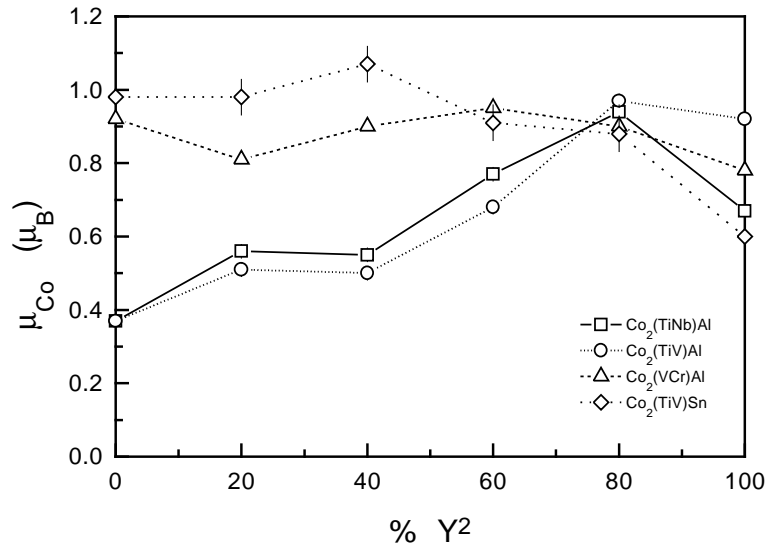
Figure 5. The local magnetic moment on Co as a function of the Y^2-element fraction in the alloys $Co_2Ti_{1-x}(V, Nb)_xAl$, $Co_2V_{1-x}Cr_xAl$ and $Co_2Ti_{1-x}V_xSn$.

a local magnetic moment.

The values of the local moment on cobalt μ_{Co} for the alloys $Co_2Ti_{1-x}V_xAl$ and $Co_2Ti_{1-x}Nb_xAl$, analogously to the values of the hyperfine field H_{Ta}, show quite similar behaviours in these two series of alloys. The μ_{Co}-values increase gradually from approximately $0.35\ \mu_B$ at $x = 0.0$ to a maximum of about $0.95\ \mu_B$ at $x = 0.8$ and then decline somewhat at $x = 1.0$, in the case of $Co_2Ti_{1-x}V_xAl$, and to a value of $0.67\ \mu_B$ in the case of $Co_2Ti_{1-x}Nb_xAl$.

The alloys $Co_2V_{1-x}Cr_xAl$ show a relatively small and somewhat irregular variation of local moment with x. The μ_{Co}-value first decreases between $x = 0$ and $x = 0.2$, increases slowly until $x = 0.6$, and then decreases again. In the case of the alloys $Co_2Ti_{1-x}V_xSn$ on the other hand the μ_{Co}-values are found to decrease rather monotonically from $x = 0.0$ to $x = 1.0$, except for the value at $x = 0.4$ which appears to be somewhat out of line even considering the experimental error.

Relatively little is known about the 3d-moment formation in the Heusler alloys, particularly the variable magnitude of the Co moment in the Co_2YZ type of alloys where Y is a non-magnetic transition element. Buschow and van Engen [8] and van Engen *et al* [9] studied the magnetic properties of a large number of Heusler alloys including the Co_2YAl and Co_2YSn alloys with the Y element varying over a large range from group IVB elements Ti, Zr, Hf to group VB elements V, Nb, Ta to the group VIB element Cr. The authors discovered a rather simple relationship between the Co moment in these alloys and the difference in the electronegativity between Co and the Y element. The value of μ_{Co} was found to decrease linearly with increasing electronegativity difference $\Delta\phi$. The observed decrease in the magnetic moment was attributed to the reduced splitting of 3d-electron bands caused by hybridization and charge transfer of 3d electrons and s, p and d electrons of the non-magnetic element Y. It was further observed [9] that the behaviour of Y elements belonging to different chemical groups is somewhat different in the Co_2YSn alloys (as compared to Co_2YAl alloys) in the respect that the straight lines representing the linear

relationship show different slopes for group IVB and VB elements.

Essentially, these results indicate that the more electronegative the Y element in Co_2YAl and Co_2YSn alloys compared to Co, the more localized are the 3d electrons, resulting in larger local magnetic moment. Since the electronegativity increases in the order $Ti < Nb < V < Cr$ [12], substitution of V, Nb for Ti or substitution of Cr for V would result in higher relative electronegativity and, as a consequence, in an increase in the local moment. An almost linear increase in the value of the local moment with increasing x expected for the alloys $Co_2Ti_{1-x}(V, Nb)_xAl$ and $Co_2V_{1-x}Cr_xAl$ is clearly not evident from the results of the present study. In particular the observed decline in the μ_{Co}-value between $x = 0.8$ and $x = 1.0$ cannot be understood within the systematics described above.

In the case of $Co_2Ti_{1-x}V_xSn$ alloys the situation is somewhat different and as can be seen from the results of van Engen *et al* [9], for the alloys of the type Co_2YSn, it is necessary to distinguish between the alloys with Y = Ti, Zr, Hf and those with Y = V, Nb. The slope of the straight line in the plot of μ_{Co} versus $\Delta\phi$ for alloys with Y = V, Nb is steeper, implying that substituting V for Ti in the $Co_2Ti_{1-x}V_xSn$ alloys should decrease the local moment on Co. The results shown in figure 5 once again do not show an expected linear decrease in the μ_{Co}-values with increasing x.
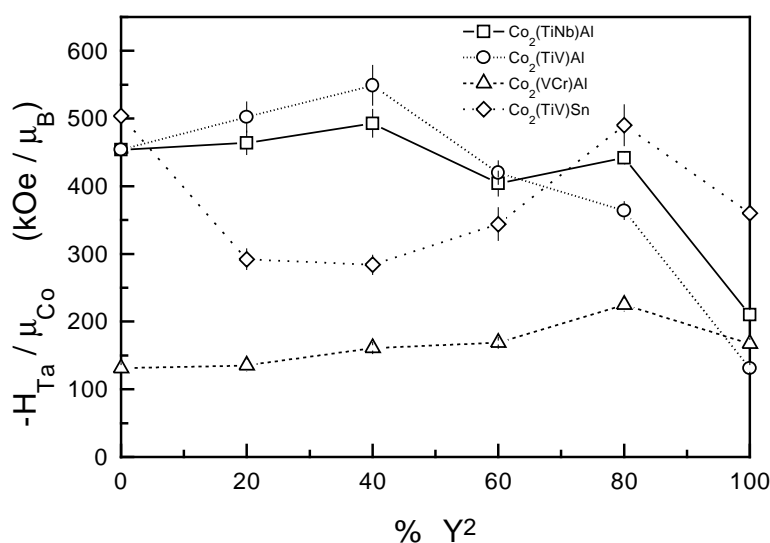

Figure 6. The reduced mhf at Ta as a function of the Y^2-element fraction in the alloys $Co_2Ti_{1-x}(V, Nb)_xAl$, $Co_2V_{1-x}Cr_xAl$ and $Co_2Ti_{1-x}V_xSn$.

We have used the μ_{Co}-values to calculate the reduced hyperfine field H_{Ta}/μ_{Co} in the series of alloys studied in the present work and the results are presented in table 1 and plotted in figure 6. The reduced mhf for the alloys $Co_2Ti_{1-x}Nb_xAl$ increases gradually between $x = 0.0$ and $x = 0.4$, decreases slightly at $x = 0.6$, and increases again between $x = 0.6$ and $x = 0.8$, and then drops rather dramatically at $x = 1.0$. The alloy $Co_2Ti_{1-x}V_xAl$ presents a similar behaviour, except that between $x = 0.4$ and $x = 0.8$ the mhf decreases gradually instead of oscillating. The reduced mhf for the alloys $Co_2V_{1-x}Cr_xAl$ on the other hand increases gradually from -131 kOe/μ_B at $x = 0.0$ to a maximum of -225 kOe/μ_B at $x = 0.8$ and then decreases to -167 kOe/μ_B at $x = 1.0$. The behaviour of the alloys $Co_2Ti_{1-x}V_xSn$ in this respect is similar to that of $Co_2V_{1-x}Cr_xAl$ except that the field

decreases rather abruptly between $x = 0.0$ and $x = 0.2$. This behaviour of the Ta field H_{Ta}/μ_{Co} in $Co_2Ti_{1-x}V_xSn$ alloys is quite different when compared with the results for the Sn fields, H_{Sn}/μ_{Co}, obtained by Dunlap and Stroink [6] from Mössbauer measurements where the authors found an almost linear decrease (the field becoming less positive) in the reduced field at Sn for $0 \leqslant x \leqslant 0.8$ and then a slight increase at $x = 1.0$. The authors concluded that their results could be explained if it is assumed that increasing the conduction electron density in Co_2TiSn (as a result of the gradual substitution of V for Ti) decreases the Sn hyperfine field. This was demonstrated by the authors by calculating the conduction electron density in this series of alloys for $0 \leqslant x \leqslant 1.0$, using the Blandin–Campbell model [13]. A similar conclusion however cannot be drawn from the results presented here for the values of H_{Ta}/μ_{Co} in these alloys since it would require the conduction electron density to increase suddenly in going from $x = 0$ to $x = 0.2$, decrease gradually until $x = 0.8$, and then increase again at $x = 1.0$. It seems obvious therefore that a simple calculation of the conduction electron density in these alloys, such as was suggested by Dunlap and Stroink [6], is inadequate for describing the Ta hyperfine-field results. The sensitivity of the Co moment to the chemical nature of the non-magnetic atoms in the Co-based Heusler alloys is quite evident from the large variations observed in the μ_{Co}-values (0.3 μ_B to 1.0 μ_B) in various alloys and it may be necessary to make elaborate band calculations in order to explain the results observed for these alloys.

A recent phenomenological calculation based on the Blandin–Campbell model [13] was reasonably successful in describing the behaviour of Ta hyperfine fields in Co-based Heusler alloys [3], especially the experimentally observed sudden drop of field when the non-magnetic transition element changed from group IVB to group VB or VIB. It was therefore expected that the present study would reveal a smooth and gradual decrease in the reduced mhf when for example Ti was replaced in a gradual manner with V or Nb in the alloy Co_2TiAl and V with Cr in the alloy Co_2VAl. The experimental results however indicate that the situation is more complex. The present results show for example (see table 1) that all of the alloys of the series $Co_2Ti_{1-x}(V, Nb)_xAl$ containing at least some Ti have high reduced-Ta-field values (ranging between -550 kOe and -400 kOe). The reduced fields for the end alloys Co_2VAl and Co_2NbAl are much lower. This could suggest that Hf(Ta) atoms have a tendency to preferentially surround themselves with Ti neighbours during high-temperature annealing as long as these are available, and this environment for some reason leads to a high reduced field. A totally random distribution of different Y atoms among the Y sites is apparently unlikely and chemical order effects may have an important role which must be considered.

Acknowledgments

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