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^{31}P nuclear magnetic resonance Knight shift and linewidth in Ni_3P and Cu_3P : a magic-angle spinning study

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Abstract. Accurate measurements of small ^{31}P Knight shift effects in crystalline Ni_3P and Cu_3P alloys have been performed by using a magic-angle spinning (MAS) nuclear magnetic resonance (NMR) technique. Both the average Knight shift and the width of its distribution have been found to be different when comparing a normal (equilibrium) and a melt-quenched Ni_3P alloy and this is attributed to possible differences in defect concentration and grain size. The ^{31}P NMR line shift of Cu_3P is much smaller ($K = 0.012\%$) than that of Ni_3P ($K = 0.179\%$) but spin–lattice relaxation time measurements indicated a Korringa-type relaxation mechanism for both alloys, i.e. Cu_3P has also a metallic character.

1. Introduction

The measurement of Knight shift effects in nuclear magnetic resonance (NMR) has a great impact on the understanding of the electronic structure of metals and alloys [1]. The Knight shift reflects the local electronic density of states (DOS) at the site of the investigated nucleus, providing unique information. However, accurate determination of the Knight shift is sometimes greatly hindered by the various mechanisms which can broaden the NMR spectrum and, thus, cause a large error in measuring the exact position of the resonance line. These mechanisms are, for example, the dipolar broadening [2] due to the direct dipolar interaction between nuclear spins or the susceptibility broadening [3].

Fortunately, these problems can be greatly overcome by using magic-angle spinning (MAS) NMR [4]. This method is based on the rapid spinning of the sample around an axis at the so-called ‘magic angle’ ($54^\circ 44'$) with respect to the static magnetic field. This sample spinning results in an averaging of the spin interaction Hamiltonians and, thus, it suppresses the majority of broadening mechanisms except for, e.g., isotropic line shift distribution, lifetime broadening and scalar indirect coupling [2, 4]. As a result, the isotropic line shift can be determined and, moreover, the intensity of the spinning sidebands can provide information about the anisotropy of the line shift tensor [5].

§ Deceased.

In spite of these benefits, there are only a few applications of the MAS NMR technique to metallic systems. The early papers of Andrew *et al* [4, 6] led to an accurate determination of the line shifts in pure metals such as aluminium and copper but no alloys were investigated by them. As a particular example, a number of studies have been performed on both crystalline and amorphous metallic hydrides using the MAS NMR technique [7–10].

In this paper, results of ^{31}P MAS NMR line shift and linewidth measurements on the crystalline Ni_3P and Cu_3P alloys will be presented. These alloys have a well known structure [11] and, thus, a better understanding of the Knight shift effects and their connection with the spatial arrangement of the lattice atoms can be expected. Moreover, the Ni_3P and Cu_3P Knight shifts can give a useful reference for the NMR studies of the crystalline and amorphous alloys such as Ni-P [12, 13] or Ni-Cu-P [14, 15]. For a more comprehensive characterisation of the electronic structure of these alloys, the ^{31}P NMR spin–lattice relaxation times have also been measured. It is noted that a preliminary account of part of the results has been given recently [10].

2. Materials and methods

The crystalline Ni_3P alloy was obtained in two different ways. First, an appropriate ratio (approximately 25 at. % P) of the powders of Ni and P were mixed. After a homogenising heat treatment, this mixture was melted and then cooled slowly to room temperature. An x-ray diffraction study of the ingot resulted in a pattern of sharp lines characteristic of crystalline materials. Four crystalline phases could be identified: tetragonal Ni_3P (strong lines), hexagonal Ni_5P_2 (weak lines), hexagonal Ni_5P_2 with axis a doubled (weak lines) and tetragonal Ni_{12}P_5 (weak lines). Part of the ingot was then crushed to powder and the Ni_3P phase in this powder is called as the normal (equilibrium) crystalline Ni_3P alloy. Second, another part of the previous bulk ingot was rapidly quenched from the melt using a single-roller melt-spinning apparatus. The resulting ribbon pieces turned out to be very brittle and could easily be powdered. The structure of this powder was found to be also crystalline by x-ray diffraction although the sharpness of the diffraction lines was reduced strongly in comparison with the slowly cooled ingot. In this melt-quenched powder, only the strong lines of the phases Ni_3P and Ni_5P_2 were observed by x-ray diffraction. The difference between the sharpness of the diffraction lines for the normal and that for the melt-quenched alloy indicates that the grain size in the latter is smaller than in the former. This is in agreement with common metallurgical experience in that rapid quenching decreases the grain size, leading even to the formation of an amorphous phase at sufficiently high cooling rates.

The crystalline Cu_3P alloy was obtained by a similar metallurgical procedure to the normal Ni_3P alloy. According to the x-ray diffractogram, the ingot contained only the Cu_3P phase. From the ingot, a powder was prepared by crushing.

For the purposes of NMR studies, the powdered alloys were mixed with a ceramic powder to provide electrical insulation between the metallic particles and, thus, to avoid the appearance of eddy currents within the sample.

The ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer equipped with a home-made probe at $H_0 = 4.7$ T; the corresponding ^{31}P NMR frequency ν_0 is 81 MHz. The spectra were obtained by Fourier transforming the echo signals generated by a $\pi/2-\tau-\pi$ pulse sequence with $\tau = 15$ μs . The length of the $\pi/2$ pulse was about 6 μs . The measurements were performed at room temperature; the spinning rates were

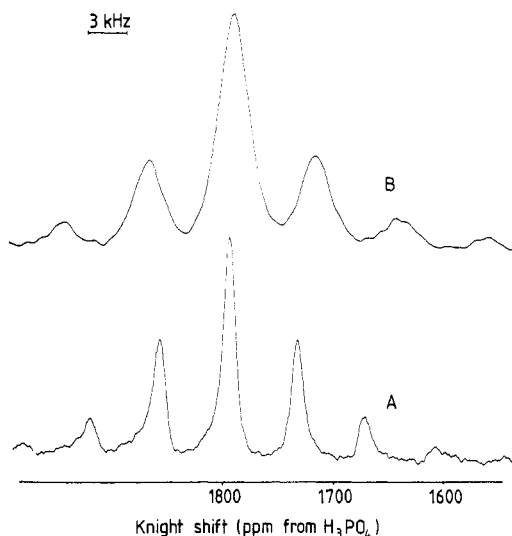


Figure 1. The ^{31}P MAS NMR spectra for normal (equilibrium) crystalline Ni_3P (curve A) and melt-quenched crystalline Ni_3P (curve B). The sample spinning rate was 3.5 kHz.

between 2.5 and 7 kHz. For the Ni_3P samples, there was no significant change in line positions and linewidths between these two limiting spinning rate values. For Cu_3P , however, acceptable spectra with clearly separated spinning sidebands could be obtained for spinning rates above 5 kHz only. The ^{31}P NMR line shifts were referred to phosphoric acid, H_3PO_4 . For the sign of the shift, the usual Knight shift sign convention was applied; at constant frequency, the line positions could be observed at a smaller external magnetic field than in H_3PO_4 which gives a positive Knight shift. The spin–lattice relaxation times were measured on non-spinning samples by the inversion recovery technique on a Bruker SXP-100 spectrometer at 2.1 T.

3. Results and discussion

3.1. Ni_3P

The ^{31}P NMR spectra could easily be observed for both the normal and the melt-quenched Ni_3P powder samples. In the slowly cooled alloy a single ^{31}P NMR spectrum was recorded both with and without sample spinning. Since the x-ray diffraction revealed that the dominant phase in this sample was Ni_3P , the observed spectrum could be ascribed to the normal Ni_3P crystalline alloy. In the melt-quenched powder, two NMR lines with an intensity ratio of about 1 : 6 were clearly resolved by using either spinning or non-spinning samples. Based on the x-ray diffraction study and the observed line position in the slowly cooled alloy, these spectra could be identified as originating from the Ni_3P (stronger signal) and Ni_5P_2 (weaker signal) phases in the melt-quenched powder (owing to the large difference in their line shifts, the association of the individual spectra with the corresponding crystalline phases is unambiguous).

The ^{31}P MAS NMR spectra of normal (equilibrium) and melt-quenched Ni_3P are presented in figure 1. The symmetrical spinning sidebands characteristic of dipolar and/or susceptibility broadening indicate the absence of considerable contributions to the linewidth due to Knight shift or chemical shift anisotropy. The corresponding isotropic

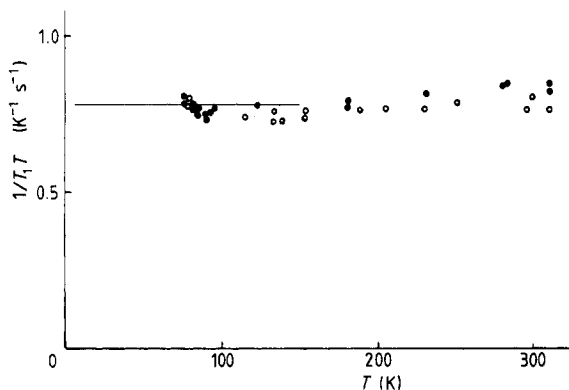


Figure 2. Temperature dependence of the ^{31}P spin-lattice relaxation rate plotted as $1/T_1T$ versus T for melt-quenched Ni_3P (○) and, for comparison, data for a normal (equilibrium) Ni_3P alloy prepared at another laboratory (—, data from [16]; ●, our measurements).

line shifts are 1793 ± 10 ppm and 1788 ± 10 ppm, respectively. (Because of susceptibility shift [7, 9], the absolute value for the frequency shift may be overestimated by about 10 ppm.) Since the chemical shift for ^{31}P in various diamagnetic insulators is of the order of some hundreds of parts per million [1], the measured line shift values of both Ni_3P alloys can be considered as predominantly due to the metallic character of the alloys, i.e. they can be identified as Knight shifts. The results of previous non-spinning NMR investigations of Ni_3P (0.17% [12] and $0.16\% \pm 0.01\%$ [16]) are reasonably close to our highly accurate ^{31}P NMR Knight shift values. Surprisingly, there is a small but significant difference between the average isotropic Knight shifts of the normal and melt-quenched samples. (The large 10 ppm error for the absolute shift determination is not valid for measuring relative shifts. Shift differences of the order of 1 ppm are significant.) Such a small shift difference obtained here by MAS NMR cannot be usually measured on metallic samples by other NMR techniques. It can be most probably attributed to a possible off-stoichiometry (nickel deficiency) of the rapidly cooled alloy owing to some quenched-in disorder. The effect can be similar to the change in the average Knight shift in various metals when alloying them with a small amount of impurities [17]. In a previous attempt [15] to produce crystalline $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{P}$ alloys with $0.1 \leq x \leq 0.5$, in some cases, phases were obtained exhibiting Knight shift values higher than that of Ni_3P ; this again can be best explained by off-stoichiometry effects (excess Ni on P sites in this case). Furthermore, approaching 25 at. % P in Ni-P amorphous alloys, the ^{31}P NMR Knight shift becomes close to that of the crystalline Ni_3P alloy [12, 13, 18], suggesting a rather similar short-range order around P atoms in both structural modifications in the vicinity of 25 at. % P. Below 25 at. % P, the ^{31}P NMR Knight shift increases with decreasing P content [12, 13, 18]; this could also be understood as caused by an increasing degree of off-stoichiometry (nickel enrichment) in a (local) structure resembling that of crystalline Ni_3P .

The metallic character of both Ni_3P alloys is further supported by the spin-lattice relaxation time T_1 data. At room temperature, we obtained $T_1 = 4.0 \pm 0.2$ ms for both the normal and the melt-quenched Ni_3P alloys (since T_1 cannot be measured as accurately as the MAS NMR Knight shift, the small difference measured for the latter cannot be observed for the spin-lattice relaxation time). A measurement of T_1 for the melt-quenched Ni_3P alloy from 77 to 300 K yielded a spin-lattice relaxation rate proportional to the temperature with a value of $1/T_1T = 0.80 \pm 0.05 \text{ K}^{-1} \text{ s}^{-1}$ (figure 2). This value is in good agreement with the results of a previous study [16, 19] where $1/T_1T =$

$0.78 \pm 0.03 \text{ K}^{-1} \text{ s}^{-1}$ was obtained from measurements on a normal (equilibrium) Ni_3P alloy in the temperature range from 4.2 to 150 K (figure 2). The temperature independence of $1/T_1T$ indicates that conduction electrons give the dominant contribution to the nuclear spin–lattice relaxation (Korringa-type relaxation).

The Knight shift and spin–lattice relaxation time was measured also for the Ni_5P_2 phase in the melt-quenched sample. The ^{31}P MAS NMR spectrum of Ni_5P_2 exhibited an asymmetry of the spinning sidebands, indicating an anisotropic Knight shift contribution. The average isotropic Knight shift was 1265 ± 10 ppm. A slightly smaller value (0.10%) was reported from non-spinning NMR measurements by Bennett *et al* [12, 18] who also gave a Knight shift value of 0.11% for the compositionally related crystalline Ni_{12}P_5 compound [18]. We found the spin–lattice relaxation time T_1 to be 8.7 ± 0.8 ms for Ni_5P_2 at room-temperature which gives $1/T_1T = 0.38 \pm 0.04 \text{ K}^{-1} \text{ s}^{-1}$. This reduced relaxation rate is in agreement with the smaller value of the Knight shift for this alloy in comparison with Ni_3P and the composition dependence of both NMR parameters (Ni_3P , 25 at.% P; Ni_5P_2 , 28.6 at.% P) reflects the decrease in DOS at the Fermi level as the P content increases [20].

The Korringa ratio [1] $k = K^2T_1T/S$ where $S = 1.605 \times 10^{-6} \text{ K s}$ for ^{31}P nuclei can be calculated to be $k = 2.6$ for both Ni_3P and Ni_5P_2 . A deviation of k from unity can be interpreted [1] as a result of the exchange enhancement of the electronic susceptibility or as an indication that not only conduction electrons with s-like character contribute to the measured values of K and T_1 . It has been concluded in recent work [20] that d-like contributions to the electronic DOS at the Fermi level prevail up to high metalloid contents in Ni–metalloid-type alloys and NMR data have also suggested [14] that in these systems the ^{31}P Knight shift K should also contain, besides a contact term K_s which is always positive, a d-type contribution K_d , which should be positive here. The $k > 1$ value obtained in the present work for the crystalline Ni_3P and Ni_5P_2 alloys suggests that the same situation should exist in these alloys as well, i.e. the d bands cannot still be completely filled. The common value of k for Ni_3P and Ni_5P_2 indicates, furthermore, that the relative importance of s- and d-like terms in the ^{31}P NMR parameters is very similar for both alloys (in spite of their significantly different magnitudes).

The MAS NMR linewidths $\delta\nu$ measured as full width at half-maximum (FWHM) of the spectra of normal and melt-quenched Ni_3P were 1.1 ± 0.1 kHz and 2.8 ± 0.1 kHz, respectively. These linewidths are greatly reduced compared with those for non-spinning samples (at 2.1 T, we obtained $\delta\nu = 8$ kHz for non-spinning normal Ni_3P [10]). The large non-spinning linewidths here are dominated by susceptibility broadening which is typical for metallic powders (especially if magnetic inhomogeneities are also present). The P–P dipolar coupling can be accounted for as a contribution of about 2 kHz [21] to the non-spinning linewidth. The dipolar broadening is almost completely averaged out by MAS since the spinning rate exceeds several times the dipolar coupling. The remainder of the susceptibility broadening contribution to the MAS NMR linewidth has not yet been fully clarified. Using the knowledge that it depends on the anisotropy of the susceptibility [22] which should be, however, weak in metals, one can expect the susceptibility broadening to be severely suppressed by MAS in the alloys investigated here.

Further contributions to the linewidth of the MAS NMR spectra can come from a distribution of the isotropic Knight shift K and from lifetime broadening. This latter effect can be estimated from the measured spin–lattice relaxation time T_1 . The resulting (Lorentzian) lifetime broadening contribution at room temperature is about 0.08 kHz. Therefore, assuming the smallness of the remnant of the susceptibility broadening, we identify the relative linewidths defined by $\delta\nu/\nu_0$ as the width δK of the isotropic Knight

shift distribution for the respective alloys and we get $\delta K \approx 13$ ppm for normal Ni_3P and $\delta K \approx 35$ ppm for melt-quenched Ni_3P . The observed difference of about 22 ppm in δK (which is, however, independent of the assumption of a negligibly small remnant broadening due to susceptibility anisotropy) indicates a broader distribution of the isotropic Knight shift in the melt-quenched sample. The quantity δK should be zero in a perfect Ni_3P crystal since all the crystallographic positions for P are equivalent in this alloy [11].

An off-stoichiometry which was assumed to explain the different average Knight shifts can also contribute to the observed linewidth difference since charge- (and spin-) density oscillations can occur around the defect sites [17]. Thus the Knight shift at the P positions will be slightly modified depending on the nucleus-defect distance and, therefore, a distribution of the isotropic Knight shift can be observed. (However since the melt-quenched alloy exhibits a smaller grain size, the effect of grain boundaries (through a similar charge-density oscillation phenomenon) on the Knight shift distribution cannot also be excluded. This latter effect has already been observed on small Pt particles [23] where it was, of course, more pronounced owing to the much smaller particle size. Both off-stoichiometry and grain boundary effects can lead to an increased MAS NMR linewidth in the melt-quenched Ni_3P alloy.)

We shall now briefly discuss the field-dependent line broadening in amorphous Ni-P alloys which exhibit broad, slightly asymmetric ^{31}P NMR lines. The dominant contributions to this large broadening of some hundreds of kilohertz at the usual NMR frequencies should be the isotropic Knight shift distribution and the anisotropic Knight shift (and its eventual distribution). In principle, they could be separated by suppressing the anisotropic contribution with the help of MAS NMR. However, because of the large total linewidth the MAS spectra recorded at the MAS spinning rates at present available show only minute changes compared with the non-spinning spectra [24]. Thus the two different kinds of the possible Knight shift contribution to the observed field-dependent broadening cannot be independently measured. However, the negligibly small narrowing upon sample spinning gives some support for the dominating role of the isotropic Knight shift distribution. Therefore the measured field-dependent contribution to the observed total linewidth in amorphous alloys can be approximately identified as the width δK of the isotropic Knight shift distribution. The $\delta K/\bar{K}$ ratio where \bar{K} is the average value of the isotropic Knight shift is 0.4 for amorphous Ni-P alloys in the vicinity of 25 at. % P [13, 25] whereas it is only 0.006 for normal (equilibrium) Ni_3P and 0.018 for melt-quenched Ni_3P .

3.2. Cu_3P

The ^{31}P MAS NMR spectrum of Cu_3P (figure 3) shows a much smaller average isotropic line shift value (123 ± 10 ppm) than that of Ni_3P . In a previous NMR study on non-spinning samples of amorphous $(\text{Ni}_{1-x}\text{Cu}_x)_{80}\text{P}_{20}$ and crystalline $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{P}$ alloys [14, 15], we have observed that, together with the conduction electron susceptibility, there is a rapid continuous decrease in the ^{31}P NMR Knight shift with increasing Cu content. Actually, in the case of Cu_3P , the ^{31}P NMR line shift is already so small that it becomes comparable with the magnitude of the ^{31}P NMR chemical shift which spans from about +250 ppm to -490 ppm in various diamagnetic compounds [1]. Some (positive) orbital contributions to the observed line shift cannot also be excluded. The decrease in the Knight shift with Cu content can be understood [14, 15] as a decrease in the d-band contribution to the DOS at the Fermi level. At the same time, with increasing Cu content

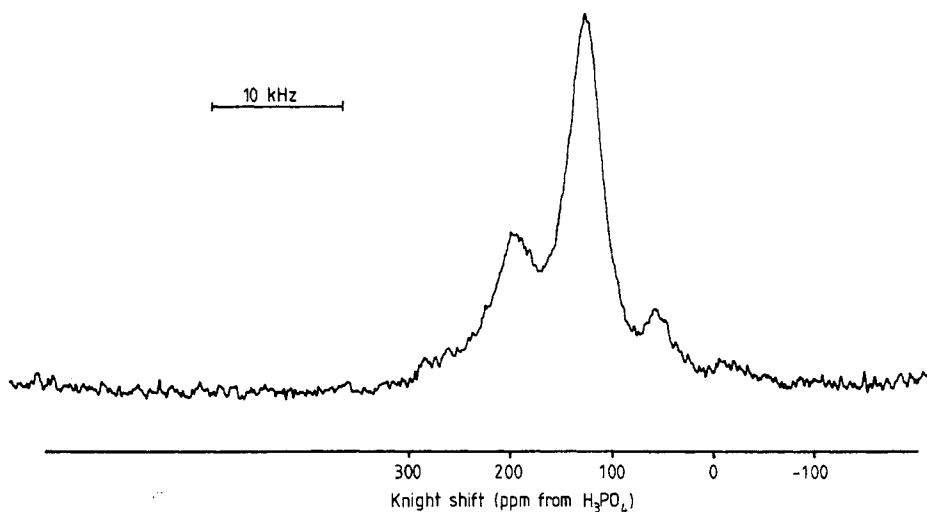


Figure 3. The ^{31}P MAS NMR spectrum of crystalline Cu_3P . The spinning rate was 6.3 kHz.

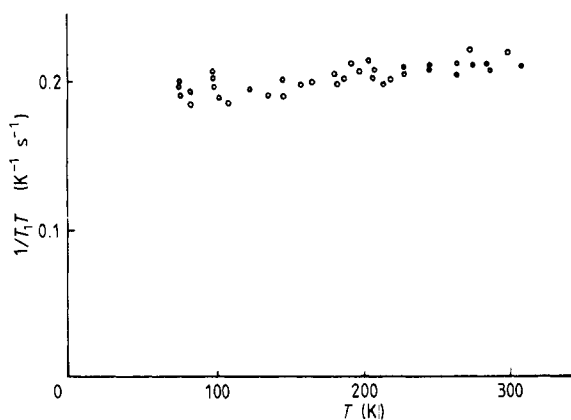


Figure 4. Temperature dependence of the ^{31}P spin-lattice relaxation rate plotted as $1/T_1T$ versus T for Cu_3P .

the total electron number also increases and the relative contribution of the s terms to the NMR parameters may eventually become stronger.

To decide about the metallic character of Cu_3P , the spin-lattice relaxation time T_1 was measured for ^{31}P nuclei from 77 to 300 K. The relaxation rate has a nearly Korringa-type temperature dependence (figure 4) with a value of $1/T_1T = 0.20 \pm 0.01 \text{ K}^{-1} \text{ s}^{-1}$ (the slight increase in $1/T_1T$ with increasing temperature can be due to some second-order effects, e.g. volume changes through thermal expansion). This means that the thermal equilibration process of the ^{31}P nuclear spins is dominated by the interaction with the conduction electrons, i.e. the Cu_3P alloy can be considered as metallic. Therefore the measured line shift definitely contains some metallic contribution (Knight shift) as well.

The Korringa ratio is calculated to be $k = 0.05$ for Cu_3P . This value is well below 1.0, indicating that the measured line shift should contain negative contributions as well. Since a ^{31}P chemical shift which would be necessary to give $k = 1$ cannot be expected

[1], this negative contribution is probably partly due to unpaired d electrons. This is in striking difference with the case of Ni_3P and Ni_5P_2 where the d contribution to the Knight shift appeared to be positive. Such a d contribution is due to a covalently transferred hyperfine interaction between phosphorus and metal sites the sign of which may be either positive or negative depending on structure and atomic components [26]. Because of lack of further data (e.g. low-temperature electronic specific heat coefficient) on the DOS of this alloy, one cannot, however, separate at present the possible contributions to the line shift for Cu_3P .

The linewidth of the main line in figure 3 is 3.4 ± 0.4 kHz which is substantially higher than that of Ni_3P . (Since for Cu_3P the room-temperature T_1 is about 16 ms, the lifetime broadening can be estimated to be 0.02 kHz which is negligibly small in this alloy.) However, there may be two more couplings of P nuclei in Cu_3P which do not exist (or negligible) for a P nucleus in Ni_3P . First, there may be a scalar indirect coupling between the P and Cu nuclei and this is left unchanged by sample spinning. Additionally, in the presence of a non-zero quadrupolar coupling of Cu nuclei, which is highly probable because of the lack of a high symmetry of Cu sites [11], the direct P–Cu coupling cannot be averaged totally by MAS NMR [27–31]. The existence of such an effect for ^{31}P – $^{63,65}\text{Cu}$ spin pairs has already been demonstrated [32].

In contrast to Ni_3P , the Cu_3P alloy exhibits a clearly visible asymmetry of the spinning sidebands. This observed asymmetry may be evaluated in terms of an anisotropic line shift tensor. (A rough estimate, using the anisotropy parameters in [5], comes to $\mu = 2.0 \pm 1.0$ and $\delta = 0.7 \pm 0.3$, where δ shows the deviation from axial symmetry and μ gives the difference between the highest (K_{33}) and lowest (K_{11}) eigenvalues of the line shift tensor. In the present case, $K_{33} - K_{11} = 155 \pm 80$ ppm is obtained.) However, we cannot establish whether the chemical shift contribution or the Knight shift contribution is anisotropic.

4. Summary

In the present paper, the results of a ^{31}P MAS NMR study of crystalline Ni_3P and Cu_3P alloys have been described. The comparison of a melt-quenched and a normal (equilibrium) Ni_3P alloy revealed a slight difference in their isotropic Knight shifts. The width of the MAS NMR spectra could be identified as the width of the isotropic Knight shift distribution which, thus, was different for these two alloys. Both effects can be explained in terms of a higher defect concentration (and, probably, a smaller grain size) of the melt-quenched Ni_3P alloy. In contrast to Ni_3P , the Cu_3P alloy exhibits a small ^{31}P Knight shift the accurate value of which is hard to determine, since the experimental line shift certainly contains a negative (diamagnetic) chemical shift term of comparable magnitude. Moreover, the ^{31}P line shift tensor in Cu_3P may be anisotropic. The metallic character of Cu_3P , however, was clearly indicated by the Korringa-type behaviour of the spin–lattice relaxation rate. The present study has demonstrated the usefulness of the MAS NMR technique in metallic alloy systems. This method enables one to measure accurately the small Knight shift effects unseen earlier.

Acknowledgments

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