Electric Field Gradient at Nb Site in the Intermetallic Compounds Nb_3X (X = Al, In, Si, Ge, Sn) Measured by PAC

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The electric field gradient (efg) at the Nb site in the intermetallic compounds Nb_3X (X = Al, In, Si, Ge, Sn) was measured by the Perturbed Angular Correlation (PAC) method using the well-known gamma-gamma cascade of 133 - 482 keV in ^{181}Ta from the β^- decay of ^{181}Hf, substituting approximately 0.1 atom percent of Nb. The PAC results show that V_{zz} drops by nearly 40% when X changes from Al to In, and by about 25% when X changes from Si to Ge and Sn. This behavior is most probably related to the change in the degree of sp hybridization in these compounds. The V_{zz} values of the studied compounds do not follow the well known universal correlation for the efg's in non-cubic metals but the observed trend is well reproduced by results of ab-initio electronic structure calculations. In the case of Nb_3Al a linear temperature dependence of the quadrupole frequencies was observed in the temperature range of 6.5 to 1210 K.

Key words: Electric Field Gradient; PAC Measurements; Nb-based Alloys; Quadrupole Interactions.

1. Introduction

The efg in non-cubic metals was extensively studied in the last two decades and is reasonably well understood [1]. For more complex compounds, like binary alloys, it is still not well understood, and a systematic experimental investigation of such compounds is of considerable interest.

The intermetallic compounds Nb_3X (X = Al, Ga, In, Si, Ge, Sn) have been extensively investigated in the past, mainly because of their interesting properties at high temperatures, such as structural strength and corrosion resistance, but also because some of them are superconducting materials. In particular, Nb_3Ge presents the highest known superconduction-temperature (T_C = 23 K) of an intermetallic compound. Nb-based alloys have a large hydrogen absorption capacity, and it is possible to prepare fine powders of these alloys by the hydriding-dehydriding cycle method. The compounds Nb_3X have a Cr_3Si type cubic structure with space group A15 and lattice parameters of about 5.2 Å. Hyperfine interaction techniques, because of their local and microscopic character, are quite suitable to investigate these compounds. A systematic study of the behavior of the efg at the Nb site in these compounds is likely to provide important information on the local charge distribution around the probe nucleus.

2. Experimental

The Nb_3X compounds were prepared by arc melting of the constituent elements (99.99%) a couple of times under an argon atmosphere and once in an Ar + 5% H_2 atmosphere along with neutron irradiated Hf substituting ~0.1 atom percent of Nb. Radioactive ^{181}Hf was produced by neutron irradiation of hafnium metal in the IEA-R1 reactor at IPEN. Crystal structures of the samples were checked by X-ray powder diffraction. The compounds Nb_3Al, Nb_3In, and Nb_3Sn presented a unique phase with A15 structure, while both Nb_3Si and Nb_3Ge contained an additional phase, which was identified as Nb_5Si_3 and Nb_5Ge_3, respectively. Hydrogenation of the sample followed by dehydrogenation produced a single-phase Nb_3Ge compound [2]. The hydrogenation was carried out by

introducing about 150 kPa of hydrogen directly into the arc-melting chamber following the last melting of the constituent elements in an Ar + 5% H_2 atmosphere. The hydrogen charging was rapid and the sample disintegrated into fine powder. Heating in a vacuum produced the dehydrogenated sample. This procedure was not effective in producing a single phase Nb_3Si sample. It continued to be a contaminated with Nb_5Si_3.

The TDPAC measurements were carried out with a conventional fast-slow coincidence set-up with four BaF_2 detectors, using the well known gamma-gamma cascade of 133 - 482 keV in ^{181}Ta from the β^- decay of ^{181}Hf. The measurements were performed at 295 K in all cases. For Nb_3Al additional measurements were carried out in the temperature range 6.5 to 1210 K. The time resolution of the system was about 0.7 ns for the gamma cascade of 133 - 482 keV.

The PAC method is based on observation of hyperfine interaction of nuclear moments with extra nuclear magnetic fields or efg's. A detailed description of this method is given in [3]. The perturbed gamma-gamma angular correlation can be expressed (neglecting the A_{44} term) as

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

where θ is the angle between the detectors, A_{22} the unperturbed angular correlation coefficient of the γ-γ cascade, and $P_2(\cos\theta)$ the Legendre polynomial. The perturbation factor $G_{22}(t)$ contains detailed information about the hyperfine interaction. In the case of a static quadrupole interaction in a polycrystalline sample and an intermediate nuclear level of the gamma cascade with spin $I = 5/2$ the perturbation factor can be expressed as

$$G_{22}(t) = S_{20} + \sum_{n=1}^{3} S_{2n}\cos(\omega_n t)\exp(-\omega_n^2\tau_R^2/2) \cdot \exp(-\omega_n^2\delta^2 t^2/2). \qquad (2)$$

The amplitude S_{2n} and the frequency ω_n depend on a nuclear quadrupole frequency ν_Q and an asymmetry parameter η defined as

$$\nu_Q = \frac{eQV_{zz}}{h} \text{ and } \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \qquad (3)$$

where Q is the quadrupole moment of the nuclear state and V_{xx}, V_{yy}, and V_{zz} are the components of the efg tensor in its principal axis system. The terms $\exp(-\omega_n^2\tau_R^2/2)$ and $\exp(-\omega_n^2\delta^2t^2/2)$ take into account the effect of a finite time resolution of the detectors τ_R and a distribution of efg around a mean value with a width δ, respectively.

The experimental perturbation function *R(t)* is calculated from measured time spectra as

$$R(t) = \sum_i f_i G_{22}^i(t) = 2\frac{W(180°, t) - W(90°, t)}{W(180°, t) + 2W(90°, t)}, \qquad (4)$$

where f_i are the relative fractions of different efg's which contribute to the PAC spectrum, each characterized by the interaction frequency ν_{Qi}, the asymmetry parameter η_i and the frequency distribution δ_i.

3. Results and Discussion

The PAC spectra of the Nb_3X compounds, measured at room temperature and their Fourier transforms are shown in Figure 1. The solid curves are the least-squares fit of the experimental data to the function given by (2). The compounds Nb_3Al and Nb_3Sn were characterized by a single quadrupole interaction with a relatively small frequency distribution ($\delta \approx 0.05$). The PAC spectrum of Nb_3In showed a principal component with ν_Q = 637 MHz and a minor fraction with ν_Q = 1006 MHz. As the X-ray data for this compound revealed only a single phase, we believe that disordered Nb sites occupied by ^{181}Hf within the Nb_3In structure may be the reason for this minor fraction. For Nb_3Ge two interaction frequencies ν_{Q1} = 751 MHz and ν_{Q2} = 197 MHz were observed, and these were assigned to the alloys Nb_3Ge and Nb_5Ge_3, respectively. As mentioned earlier, a cycle of hydrogenation and dehydrogenation produced a pure sample of Nb_3Ge with A15 structure and resulted in a PAC spectrum with a unique frequency of ν_Q = 773 MHz. In the case of Nb_3Si, the PAC data could be fitted with three frequencies with a major component at ν_{Q1} = 986 MHz, and minor ones at ν_{Q2} = 800 MHz and ν_{Q3} = 151 MHz. We assign the major fraction to Nb_3Si, considering a similarity with Nb_3Ge in the value of η, and associate the two minor fractions with the hexagonal ($P6_3/mcm$) and tetragonal (I4/mcm) phases of the alloy Nb_5Si_3, which have η values close to zero.

Experimentally determined hyperfine parameters ν_Q, V_{zz} and η as well as the crystal lattice parameter a of the studied alloys are given in Table 1. The

Table 1. Lattice constant, hyperfine parameters, experimental and calculated values of V_{zz} and electronic enhancement factor α for the studied Nb_3X compounds.

Compound	a [Å]	ν_Q [MHz]	η	V_{zz}^{exp} [10^{22} V/m^2]	$(1-\gamma_\infty)V_{zz}^{latt}$ [10^{22} V/m^2]	$\alpha = \lvert V_{zz}^{exp}/V_{zz}^{ion}\rvert$	$V_{zz}^{ab\text{-}initio}$ [10^{22} V/m^2]
Nb_3Al	5.186	1077(3)	0.21(1)	1.887(5)	3.793	0.50	1.373
Nb_3In	5.293	637(4)	0.41(2)	1.116(7)	3.550	0.31	
Nb_3Si	5.155	986(2)	0.39(1)	1.728(4)	3.448	0.41	1.105
Nb_3Ge	5.169	773(2)	0.34(1)	1.354(4)	3.408	0.40	0.835
Nb_3Sn	5.289	767(3)	0.36(1)	1.347(5)	3.193	0.42	

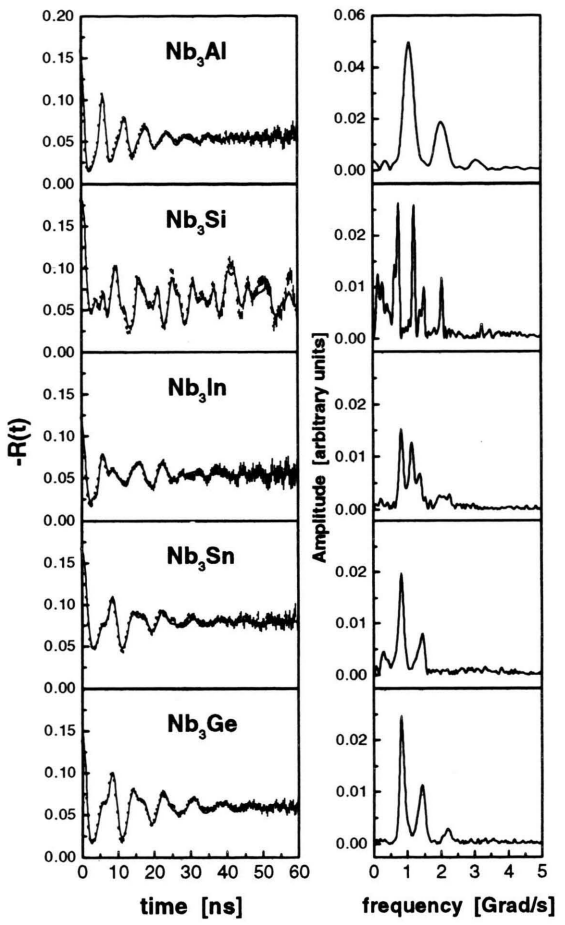

Fig. 1. PAC spectra and corresponding Fourier transforms for Nb_3X compounds at room temperature.

values of V_{zz} were determined from the observed quadrupole frequencies using the known value of the quadrupole moment of the 482 keV state in ^{181}Ta, Q = 2.36 b [4]. The results given in Table 1 show that the V_{zz} drops by approximately 40% when a group IIIA element Al (3sp), is replaced by another group IIIA element In (5sp) in the Nb_3X compounds. A similar drop (~25%) is observed when a group IVA element Si (3sp) is replaced by another group IVA element Ge (4sp) or Sn (5sp). This could be explained in part by an increase in the value of the lattice parameter in going from Al to In and also in going from Si to Ge and Sn (see Table 1). However, electronic effects like changes in the degree of sp hybridization in these compounds are expected to dominate the observed trends [5].

From a phenomenological point of view, the efg at a nuclear site is assumed to be the sum of two contributions, the lattice efg, representing the ionic contribution from the neighboring ions in a non-cubic lattice and the electronic efg, from the extra ionic electrons [6]:

$$V_{zz} = (1-\gamma_\infty)V_{zz}^{latt} + V_{zz}^{el}. \tag{5}$$

The lattice contribution V_{zz}^{latt} is amplified by the Sternheimer antishielding factor $(1-\gamma_\infty)$ which accounts for the inner atomic shell polarization. The ionic contribution can easily be determined by the usual lattice sum method, which in the present work was performed by using the simple Point Charge Model (PCM) and the value of $(1-\gamma_\infty) = 62$ for Ta [7]. The electronic contribution is more difficult to determine, requiring ab-initio band structure methods.

Raghavan *et al.* [8] discovered a universal correlation between electronic and ionic contributions to the efg for several non-cubic metal hosts and found that for moderate values of the ionic component, $V_{zz}^{ion} = V_{zz}^{latt}(1-\gamma_\infty)$, the extra-ionic component is proportional to it and has an opposite sign, $V_{zz}^{el} = -KV_{zz}^{ion}$, where K is a positive constant of the order of 2 - 5, depending on the host lattice and impurities. One can thus write for the efg at a nuclear site

$$V_{zz} = (1-\gamma_\infty)V_{zz}^{latt}(1-K). \tag{6}$$

The ratio $\alpha = |1-K| = |V_{zz}/V_{zz}^{ion}|$, scaling from 1 to 4, is the so-called electronic enhancement factor. It is a good parameter to evaluate the electronic contribu-

tion to the efg. The values of α for the Nb_3X alloys, shown in Table 1, are of the order of 0.4. It appears therefore that these alloys do not follow the universal correlation, which is well known in the case of many non-cubic metals.

The efg at the Nb site in Nb_3Al, Nb_3Si and Nb_3Ge has also been computed by ab-initio electronic structure calculations with the FP-LAPW method embodied in the WIEN97 code [12]. The results of these calculations, shown in the last column of Table 1, reproduce well the trends of the experimental data, although not the absolute EFG values, which are smaller by 25 - 35%. The difference can not be assigned directly to effects due to the foreign Ta probe atoms in these compounds, since similar discrepancies, giving smaller calculated values, are also observed for the V_3X compounds [5], where the probe atoms were not impurities.

The temperature dependence of the quadrupole frequency ν_Q was measured in the case of Nb_3Al in the range of 6.5 to 1210 K. A plot of $\nu_Q(T)/\nu_Q(0)$ versus T, shown in Fig. 2, indicates a linear temperature dependence. The solid line is the least squares fit of the data to the function

$$\nu_Q(T) = \nu_Q(0)(1 - BT), \tag{7}$$

where $\nu_Q(0)$ is the quadrupole frequency at $T = 0$ K. The fitted parameter B was found to be $1.18(1) \times 10^{-4}$ K^{-1} which is of the same order of magnitude as for other binary compounds that do not follow the universal correlation [9, 10]. The temperature dependence of the electric quadrupole interaction for non-cubic metals follows a simple $T^{3/2}$ relation [11].

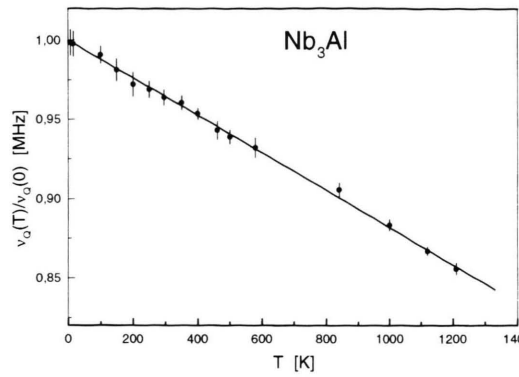

Fig. 2. The temperature dependence of the quadrupole frequency in Nb_3Al compound.

This $T^{3/2}$ law is not yet understood quantitatively, but it is attributed to thermal lattice vibrations. A linear temperature dependence of the quadrupole frequency ν_Q was reported for Zr_2Fe and Zr_2Co alloys [10] and was associated with a phonon mode softening of the lattice vibrations. Superconducting materials present this kind of lattice vibration, resulting from the coupling of charge density waves to the lattice.

PAC measurements to study the influence of hydrogen absorption in Nb_3X compounds are in progress in our laboratory, especially to investigate the possibility of the presence of dynamic electric quadrupole interactions.

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[1] E. N. Kaufmann, Hyp. Int. **9**, 219 (1981).
[2] X. Li, A. Chiba, and S. Takahashi, J. Mater. Res. **13**, 2526 (1998).
[3] E. Karlsson, E. Matthias, and K. Siegbhan, Perturbed Angular Correlations; North-Holland, Amsterdam 1964.
[4] T. Butz and A. Lerf, Phys. Lett. **97A,** 217 (1983).
[5] H. Haas, Book of Abstracts of "11th International Conference on Hyperfine Interactions", Durban, South Africa, August 23 - 28, 1998, p. Mo05.
[6] R. E. Watson, A. C. Gossard, and Y. Yafet, Phys. Rev. **A 140,** 375 (1965).
[7] P. Raghavan, E. N. Kaufmann, R. S. Raghavan, E. J. Ansaldo, and R. A. Naumann, Phys. Rev. **B13,** 2835 (1976).
[8] R. S. Raghavan, E. N. Kaufmann, and P. Raghavan, Phys. Rev. Lett. **34,** 1280 (1975).
[9] P. Wodniecki, B Wodniecka, M, Marszalek, and A. Z. Hrynkiewicz, Z. Naturforsch. **51a,** 437 (1996).
[10] M. Marszalek, H. Saitovitch, P. R. J. da Silva, and A. Z. Hrynkiewicz, J. Alloys Comp. **219,** 132 (1995).
[11] J. Christiansen, P. Heubes, R. Keitel, W. Klinger, W. Loeffler, W. Sandner, and W. Witthuhn, Z. Physik **B24,** 177 (1976).
[12] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology 1997. (Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59,** 399 (1990).)