NMR study of *p*-type half-Heusler thermoelectric $Nb_{1-x}Ti_xFeSb$

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Abstract

To investigate the local behavior of defects and mixed compositions in NbFeSb-based semiconductors, for improved thermoelectric efficiency, we have performed ^{93}Nb and ^{121}Sb NMR, as well as Mössbauer measurements, on pure NbFeSb and a series of *p*-type Ti-substituted (Nb,Ti)FeSb samples with different substitution levels. A small but consistently increasing paramagnetic defect density is observed with the increase of Ti substitution level revealing the existence of additional Ti-induced paramagnetic defects. NMR line shapes show a clear difference between effect of intrinsic and extrinsic defects in NbFeSb. The NMR shifts can be well understood by a model combining a Knight shift and composition-dependent chemical shift. The results indicate a nearly rigid-band behavior for the valence band with a small enhacement of effective mass vs substitution. For pure NbFeSb samples, the Mössbauer spectra include an additional *T*-dependent singlet. The increase of its area can be explained based on carriers activated into a shallow acceptor-like defect level above the valence band, consistent with the defect activation results obtained with NMR. In samples with Ti substitution, the Mössbauer spectra are consistent with a random neighbor distribution, indicating no preferential local ordering.

Outline

1. Introduction to half-Heusler and nuclear magnetic resonance
2. NMR Shifts

   Large susceptibility; interaction effects.
3. Spin-lattice relaxation (T_1)

   Measure of hole behavior; resonant states
4. Conclusion

Tian *et al.*, "Defect charging and resonant levels in half-Heusler $Nb_{1-x}Ti_xFeSb$", arXiv:1912.09643.

Introduction

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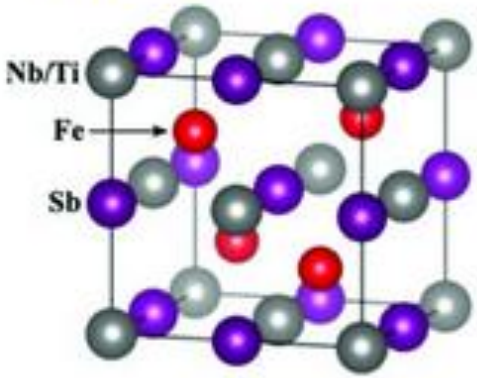
- Half-Heusler: $ZT > 1.5^{*}$
- NbFeSb: Power factor >= 100 μW cm^{-1} K^{-2}
- This work: $Nb_{1-x}Ti_xFeSb$
  - x = 0, 0.05, 0.1, 0.2, 0.3
  - Cation(Ti^{+}) substitution → p-type
  - p: measured carrier concentration



x	label	Actual composition	p (10^{20} cm^{-3})	p_{theo} (10^{20} cm^{-3})	p/p_{theo}
0	NbFeSb-1050	NbFeSb[a]	0.9[a]	-	-
0.05	Ti(0.05)	$Nb_{0.94}Ti_{0.05}Fe_{1.01}Sb_{0.99}$[b]	8.1[b]	9.5	0.85
0.1	Ti(0.1)	$Nb_{0.89}Ti_{0.1}Fe_{1.00}Sb_{0.99}$[b]	15.2[b]	19	0.80
0.2	Ti(0.2)	$Nb_{0.8}Ti_{0.2}Fe_{1.02}Sb_{0.99}$[b]	25.7[b]	38	0.68
0.3	Ti(0.3)	$Nb_{0.69}Ti_{0.3}Fe_{1.02}Sb_{0.98}$[b]	30.3[b]	57	0.40

* H. Zhu et al. Nat. Commun. 10, 270(2019)

Nuclear magnetic resonance (NMR)

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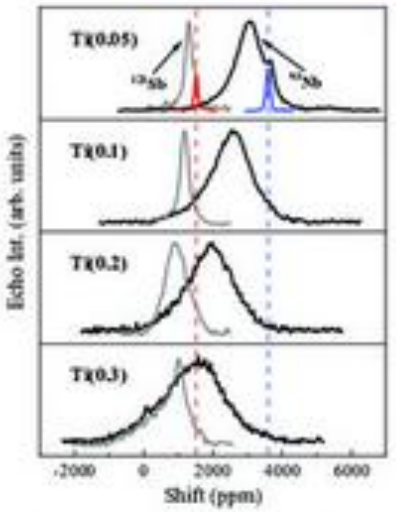
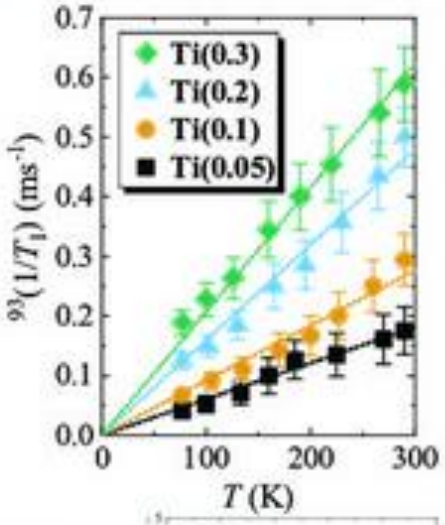
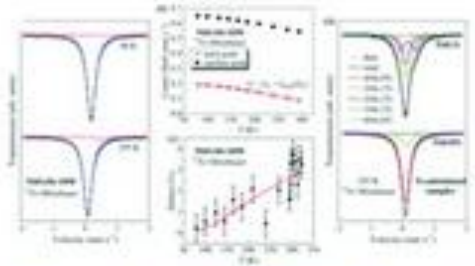
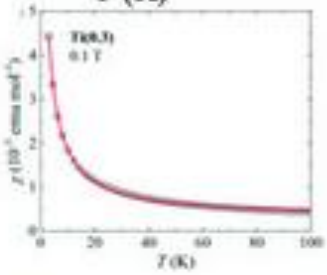
- Shift:
  - Chemical shift: local electronic environment
  - Knight shift (K): conduction electrons
- Spin-lattice relaxation time (T_1):
  - recovery of nuclear magnetization.
- Other methods:
  - Magnetic measurements *
  - Mossbauer spectra *
  - DFT









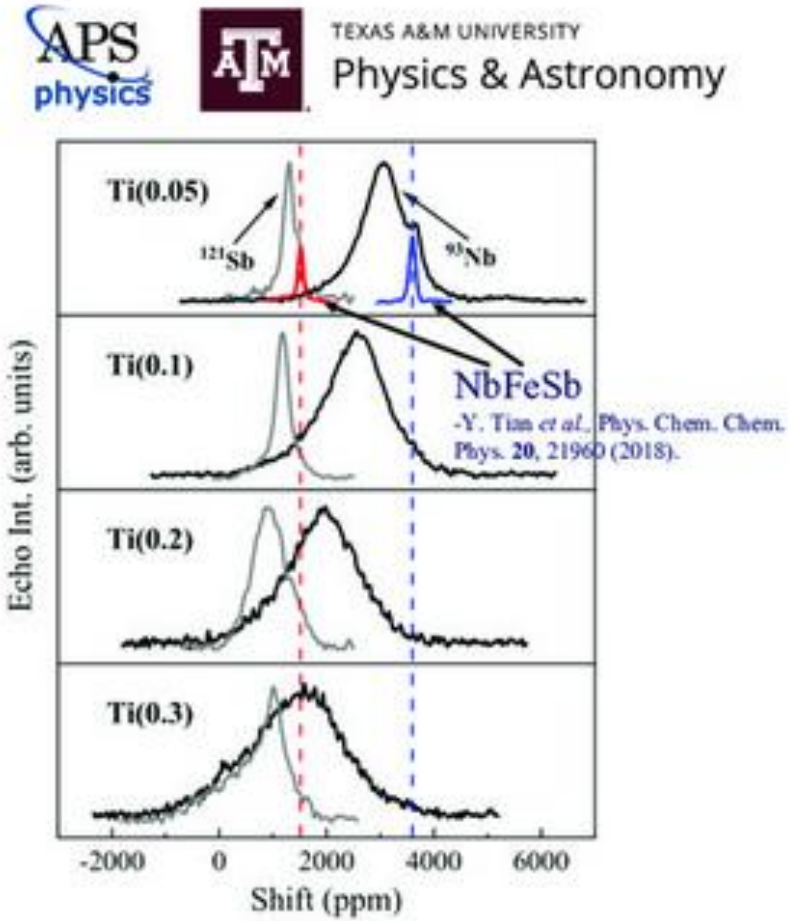
Yefan Tian et al., "Defect Charging and Resonant States in half-Heusler Nb1-xTixFeSb", arXiv preprint.

Line shape

- Line width:
  - x = 0.05, 0.1, 0.2, 0.3
  - Superposition of local environments at Nb and Sb sites
- Line shape:

  As x increases, both ^{93}Nb and ^{121}Sb:
  - Broader
  - Move to lower frequencies

    (Shifts analyzed as spectrum-weighted mean shift = first moment.)



Shift fitting

- Knight shift (K) can be summarized as:

$$K = \frac{H_{\mathrm{HF}}\chi_{\mathrm{p}}}{\mu_{\mathrm{B}}} = g_{\mathrm{partial}}\,(E_{\mathrm{F}})\left(\frac{g_{\mathrm{eff}}}{2}\right)\mu_{\mathrm{B}}H_{\mathrm{CP}}$$

- d-electron core polarization: $H_{\mathrm{HF}} \rightarrow H_{\mathrm{CP}}$
- Effective mass approximation:

$$g_{\mathrm{partial}}(E_F) = m_{\mathrm{eff}}\frac{(3\pi^2)^1}{\pi^2\hbar^2}p^{1/3}$$

- Chemical shift $\delta \propto x$ + const. *
- Total shift = $K + \delta = A[p(x)]^{1/3} + Bx + C$

* K. Beshah et al., Phys. Rev. B **36**, 6420 (1987).

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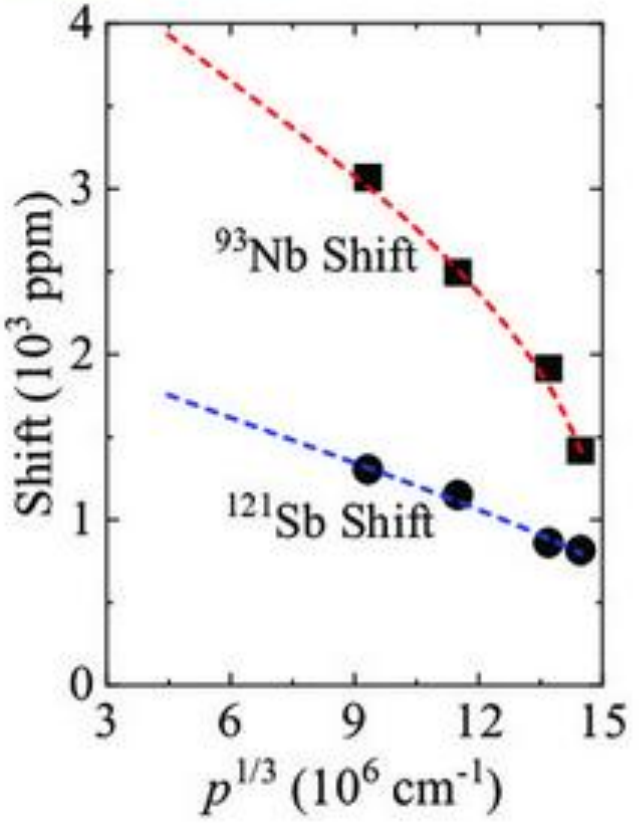
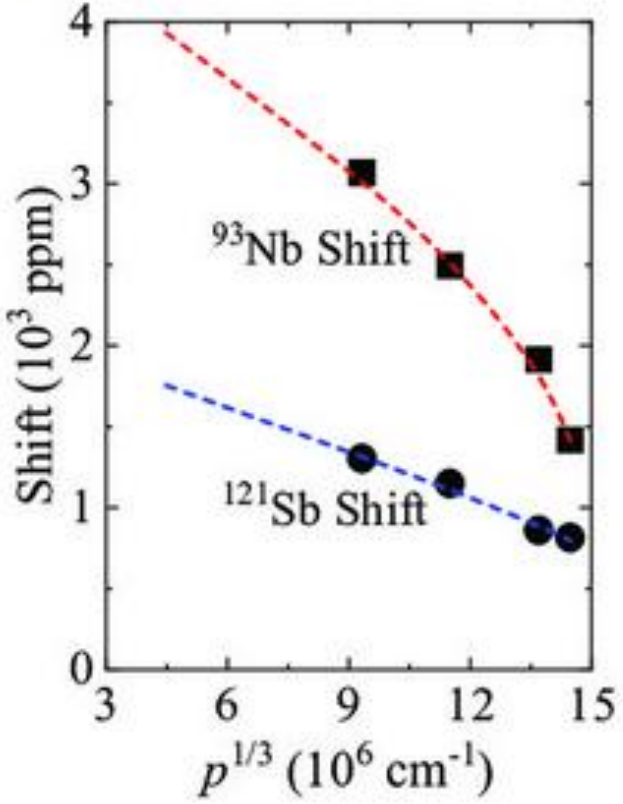


Chemical shift

- ^{93}Nb:
  - $\delta(x=0)$ = 4700 ppm, decreasing rapidly with x
  - DFT results: 3220 ppm
  - related to Van-Vleck susceptibility *
    - electron-electron interactions enhanced
- ^{121}Sb:
  - Also large x=0 shift: 2200 ppm

DFT calculations: Wien2k package
PBE potential, experimental lattice constants



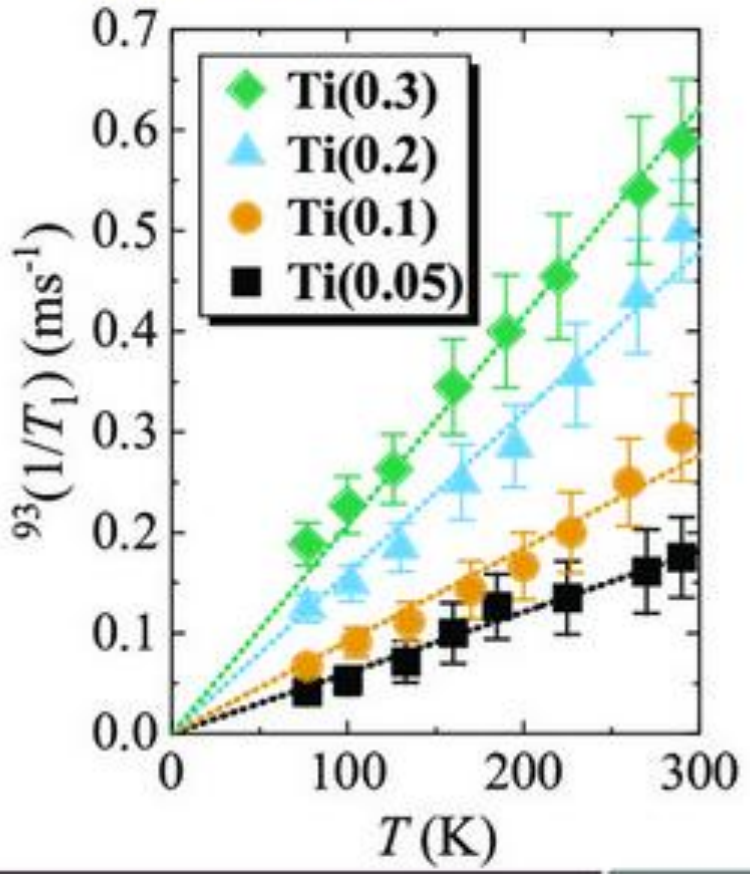
* H. Kontani and K. Yamada, J. Phys. Soc. Jpn. **65**, 172 (1996)

^{93}Nb Spin-lattice relaxation $^{93}(1/T_1)$

- Model for recovery of the ^{93}Nb central-transition magnetization:

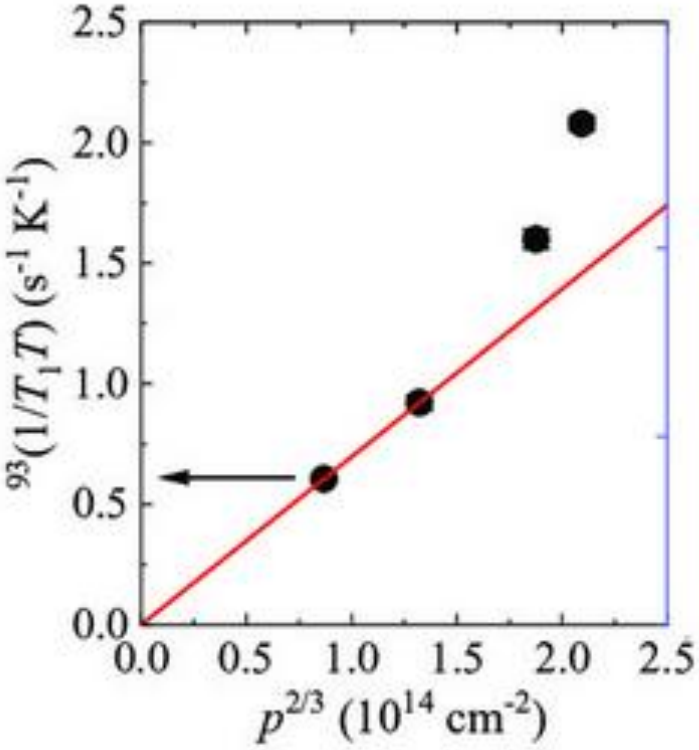
$$\frac{M(t)-M(\infty)}{M(\infty)} = -2\alpha(0.152e^{-\frac{t}{T_1}} + 0.14e^{-\frac{6t}{T_1}} + 0.153e^{-\frac{15t}{T_1}} + 0.192e^{-\frac{28t}{T_1}} + 0.363e^{-\frac{45t}{T_1}}).$$

- $M(t)$: measured signal at the recovery time t.
- Fit recovery curve → T_1 versus T
- Constant T_1T:
  - metallic-type relaxation process



^{93}Nb Spin-lattice relaxation (T_1)

- **Two contributions:**
  - Spin moments of conduction electron
  - Orbital contribution
  - $(1/T_1)_{total} = (1/T_1)_{orb} + (1/T_1)_d$
- **Orbital** found to dominate:
  - $(1/T1)_{orb} = 2A(2\pi/\hbar)[\gamma_e\gamma_n\hbar^2 g_{Nb}(E_F)\langle r^{-3}\rangle]^2 k_B T$
  - A: d-orbital degeneracy factor
    - A= 9.8 from DFT
  - Fit for low x:
    - $m_{eff} = 4.6\ m_e$
    - DFT result: $m_{eff} = 4.9\ m_e$



^{93}Nb Spin-lattice relaxation (T_1)

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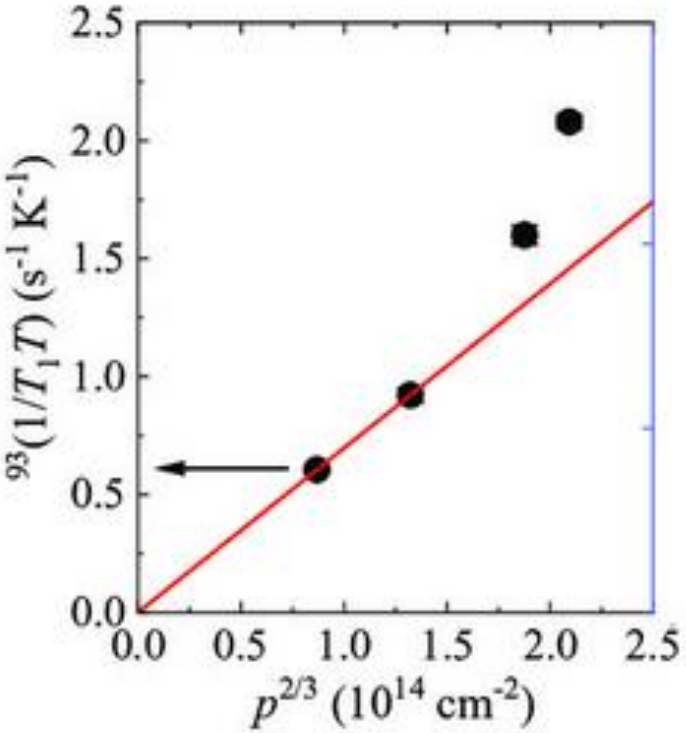
- **Spin part:**
  - Core-polarization contribution
  - d-spin

    $(1/T_1)_d = 2hk_BT[\gamma_n H_{CP} g_{Nb}(E_F)]^2 q$

  - Result:

    $(1/T_1T)_d = 0.016\ s^{-1}\ K^{-1}$

    Much smaller than orbital contribution



^{93}Nb Spin-lattice relaxation (T_1)

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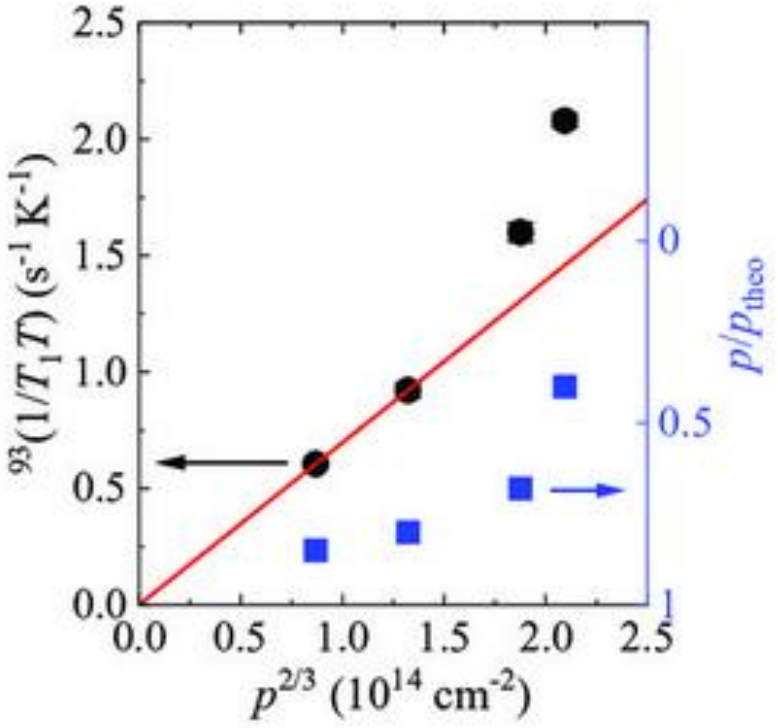
- **Result:**
  - $1/T_1 \propto [g(E_f)]^2 \propto p^{2/3}$
  - Good agreement low p
  - Upturn for large p
- Also p/p_{theo} departure for large p



^{93}Nb Spin-lattice relaxation (T_1)

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- **Result:**
  - $1/T_1 \propto [g(E_f)]^2 \propto p^{2/3}$
  - Good agreement low p
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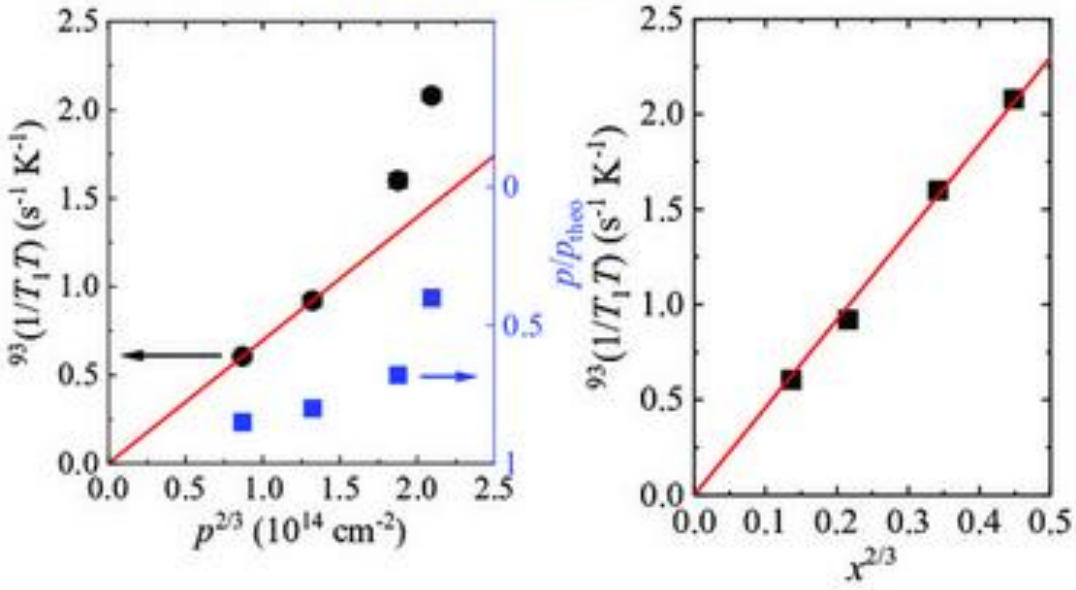
- Also p/p_{theo} departure for large p
- $1/T_1T$ vs x:
  - carriers contributing to $1/T_1$ not contributing to Hall
  - likely model: Resonant VB states at large x.



Conclusions

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a. Information about band-edge states for substituted NbFeSb.
b. NMR shifts well-explained by model combining Knight shift and chemical shift.
c. Van-Vleck susceptibility enhanced: electron-electron interaction contribution.
d. T_1 analysis reveals p/p_{theo} discrepancy: resonant states

Tian *et al.*, "Defect charging and resonant levels in half-Heusler $Nb_{1-x}Ti_xFeSb$", arXiv:1912.09643.

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