

NMR study of *p*-type half-Heusler thermoelectric $\text{Nb}_{1-x}\text{Ti}_x\text{FeSb}$

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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 enhancement 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



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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.](#)

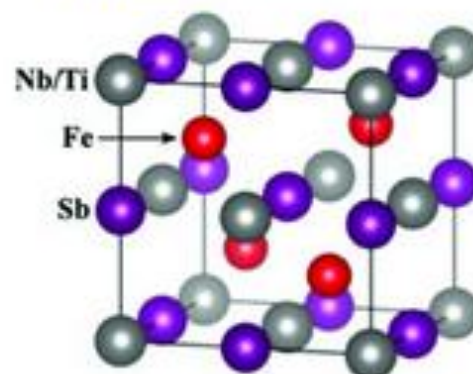
Introduction



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- Half-Heusler: $ZT > 1.5^*$
- NbFeSb: Power factor $\geq 100 \mu\text{W cm}^{-1} \text{K}^{-2}$
- This work: $\text{Nb}_{1-x}\text{Ti}_x\text{FeSb}$
 - $x = 0, 0.05, 0.1, 0.2, 0.3$
 - Cation(Ti^+) substitution \rightarrow 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

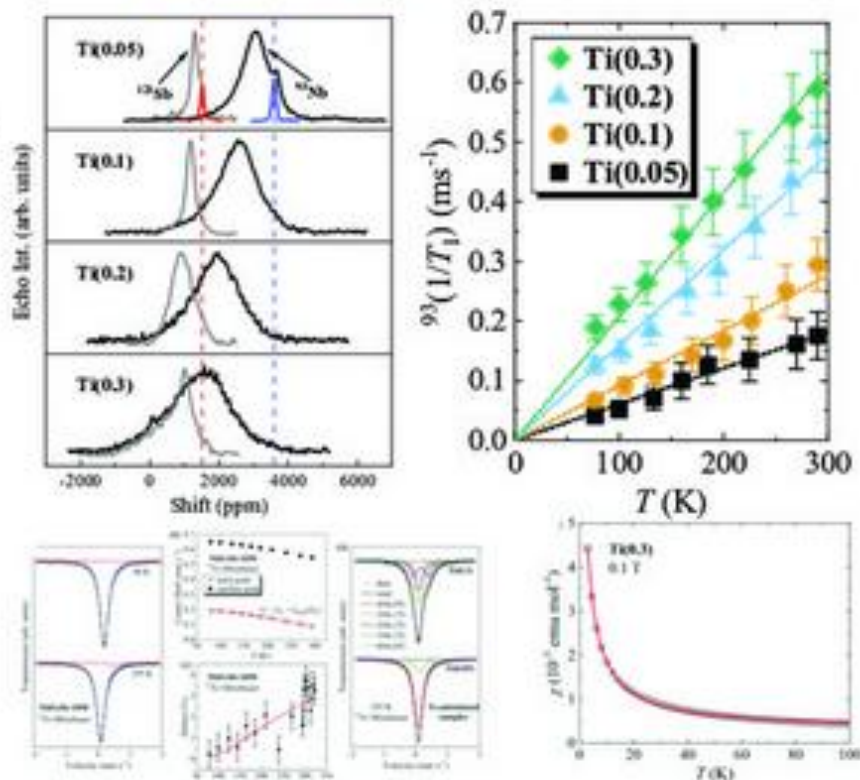
* H. Zhu et al. Nat. Commun. 10, 270(2019)

Nuclear magnetic resonance (NMR)



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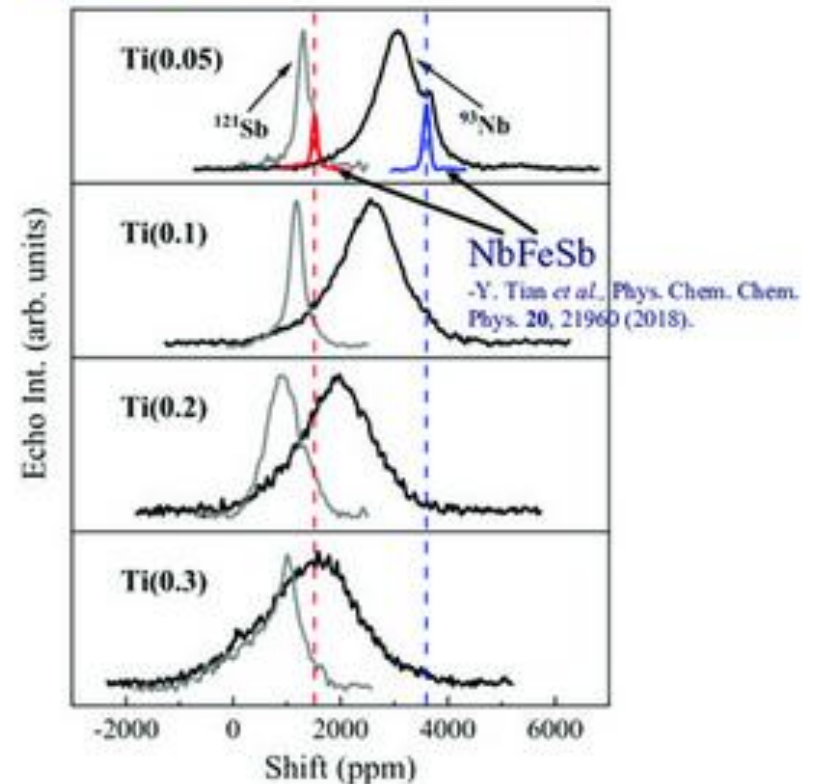
- Shift:
 - Chemical shift: local electronic environment
 - Knight shift (K): conduction electrons
- Spin-lattice relaxation time (T_1):
 - recovery of nuclear magnetization.
- Other methods:
 - Magnetic measurements
 - Mossbauer spectra
 - DFT



Yefan Tian et al., "Defect Charging and Resonant States in half-Heusler Nb_{1-x}Ti_xFeSb", 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:

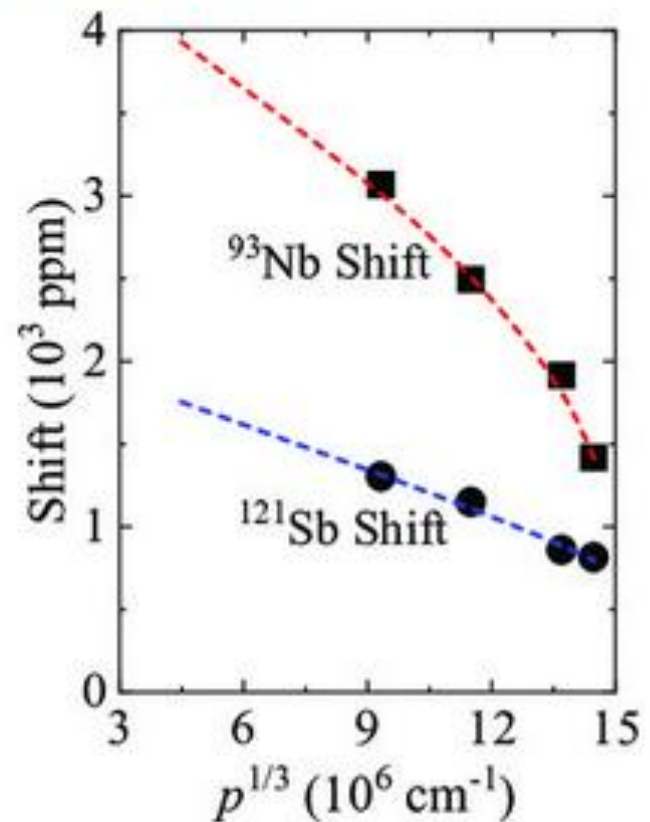
$$K = \frac{H_{\text{HF}}\chi_p}{\mu_B} = g_{\text{partial}}(E_F) \left(\frac{g_{\text{eff}}}{2}\right) \mu_B H_{\text{CP}}$$

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

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

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

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

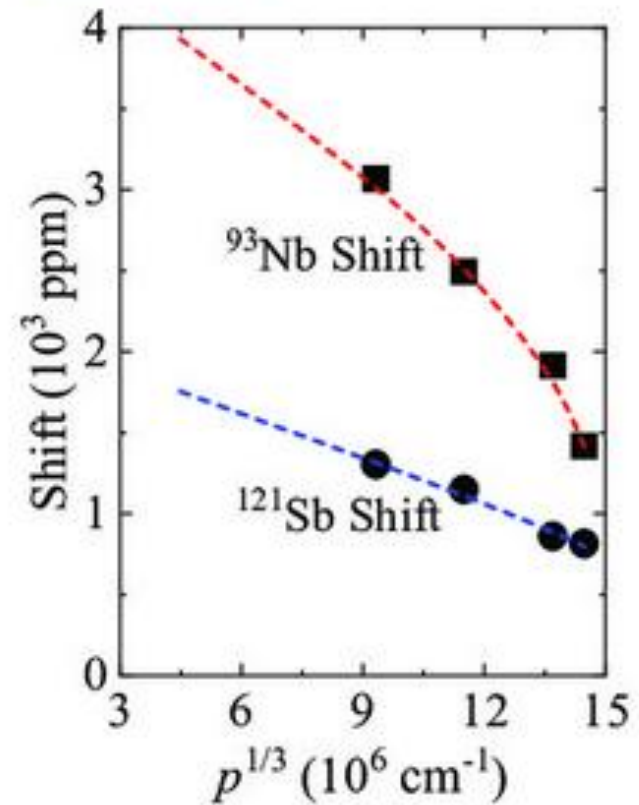


Chemical shift

- ^{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)

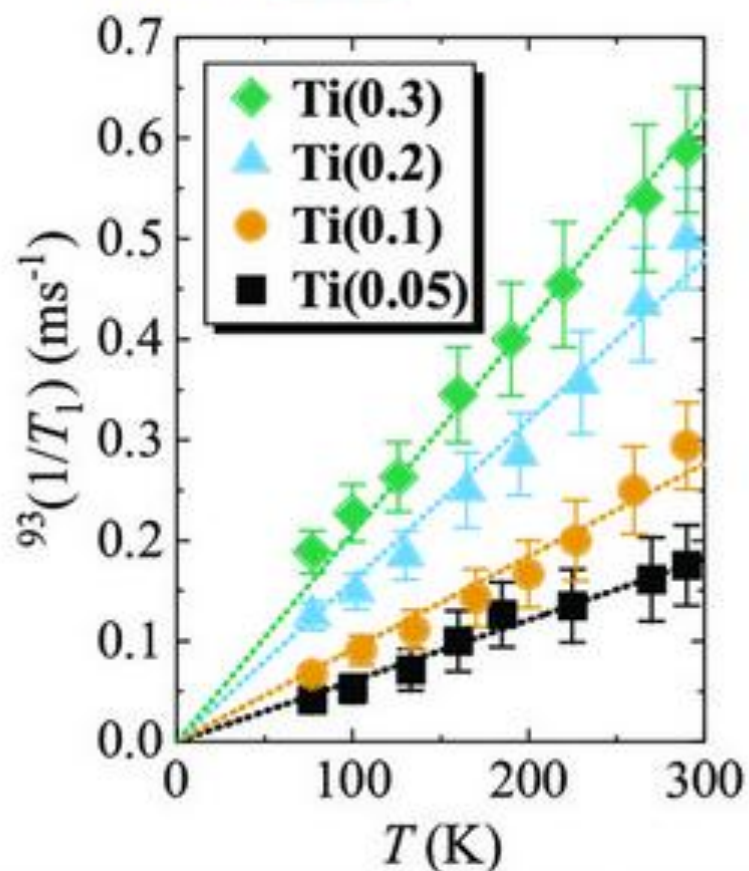


^{93}Nb Spin-lattice relaxation $^{93}(1/T_1)$

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

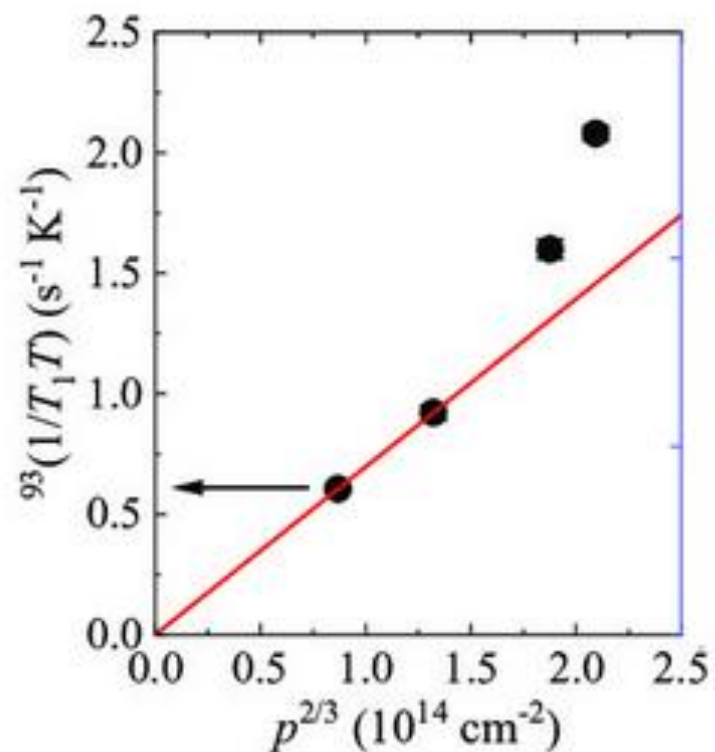
$$\frac{M(t) - M(\infty)}{M(\infty)} = -2\alpha(0.152e^{-\frac{t}{T_1}} + 0.14e^{-\frac{2t}{T_1}} + 0.153e^{-\frac{3t}{T_1}} + 0.192e^{-\frac{3t}{T_1}} + 0.363e^{-\frac{4t}{T_1}}).$$

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



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

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



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

- Spin part:

- Core-polarization contribution

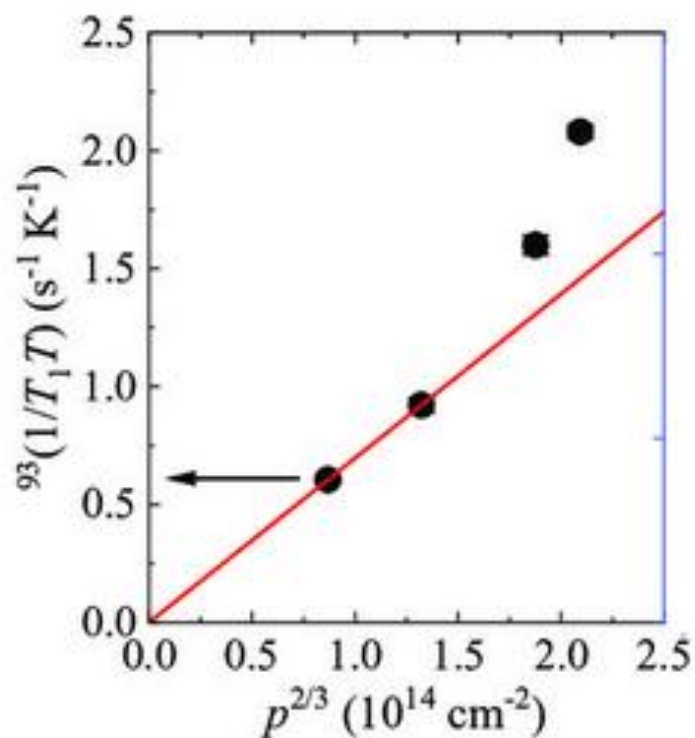
- d-spin

$$(1/T_1)_d = 2hk_B T [Y_n H_{CP} g_{\text{Nb}}(E_F)]^2 q$$

- Result:

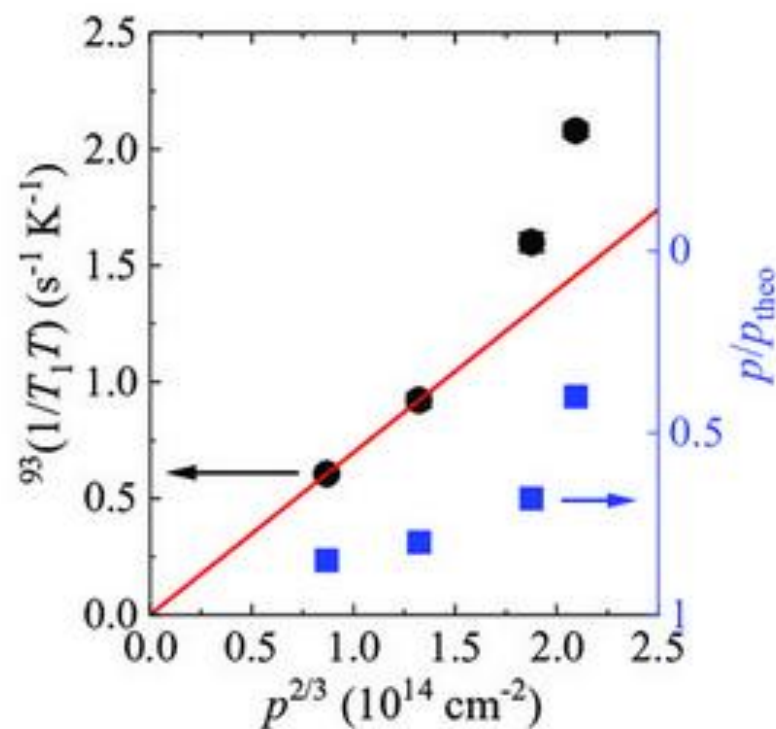
$$(1/T_1 T)_d = 0.016 \text{ s}^{-1} \text{ K}^{-1}$$

Much smaller than orbital contribution



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

- 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

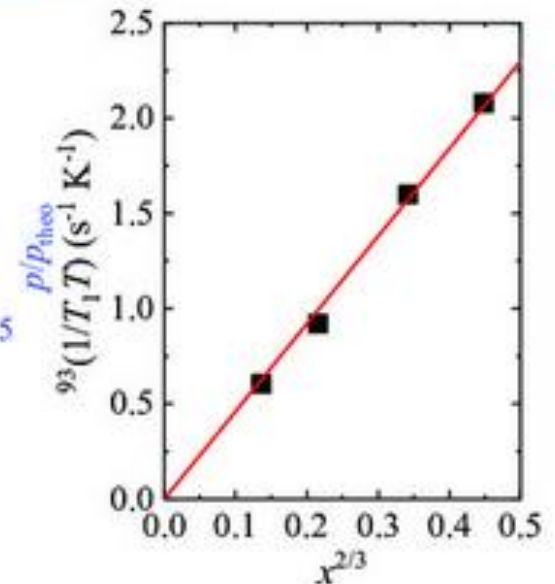
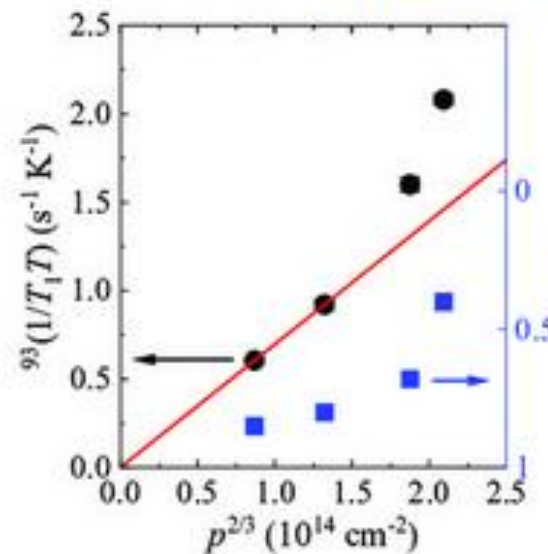


^{93}Nb Spin-lattice relaxation (T_1)



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- **Result:**
 - $1/T_1 \propto [g(E_f)]^2 \propto p^{2/3}$
 - Good agreement low p
 - Upturn for large p
- Also p/p_{theo} departure for large p
- $1/T_1 T$ 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_yFeSb”, arXiv:1912.09643.](#)

Acknowledgements:

