

## Suppression of Angular Momentum Transfer in Cold Collisions of Transition Metal Atoms in Ground States with Nonzero Orbital Angular Momentum

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The Zeeman relaxation rate in cold collisions of Ti( $3d^24s^2\ ^3F_2$ ) with He is measured. We find that collisional transfer of angular momentum is dramatically suppressed due to the presence of the filled  $4s^2$  shell. The degree of electronic interaction anisotropy, which is responsible for Zeeman relaxation, is estimated to be about 200 times smaller in the Ti-He complex than in He complexes with typical non- $S$ -state atoms.

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The interaction potential between atoms in states with nonzero orbital angular momentum is anisotropic [1]. The electronic interaction anisotropy drives inelastic energy and angular momentum transfer in atomic collisions. This anisotropy is of fundamental importance for cooling mechanisms in interstellar clouds [2], Zeeman predissociation of van der Waals complexes [3], energy level structure of weakly bound molecules [4], and in determining whether an atomic species can be evaporatively cooled in a magnetic trap. Electronic interaction anisotropy may lead to novel properties of quantum degenerate gases [5].

In this Letter we show that the interaction anisotropy in complexes involving non- $S$ -state transition metal atoms is dramatically suppressed. The unfilled  $d$  shell of such atoms is surrounded by an outer filled  $s$  shell so we term it “submerged.” Our measurement and theory show that the presence of the  $s$  shell makes these atoms interact with a collision partner effectively like an  $S$ -state atom, even though they carry a large internal angular momentum. This opens up a possibility for the creation of degenerate gases with non- $S$ -state transition metal atoms, as well as adding to our fundamental understanding of anisotropic atomic interactions.

One of the most widely used cooling methods, evaporative cooling of magnetically trapped atoms, rests upon elastic collisions that drive evaporation and cooling and inelastic Zeeman relaxation that results in heating and trap loss. The effect of inelastic loss on evaporative cooling efficiency and condensate lifetimes can be parametrized by a single number  $\gamma$ , the ratio of elastic and inelastic collision rates. Depending on the value of  $\gamma$ , evaporative cooling and condensation can be straightforward ( $\gamma \geq 10^4$ ) or impossible ( $\gamma \leq 10$ ) [6]. The value of  $\gamma$  is determined by the interaction anisotropy. When one or both of the atoms are in electronic states with nonzero electronic orbital angular momentum (non- $S$ -state atoms), the electronic interaction anisotropy couples the rotational motion of the collision complex with the atomic angular momentum [1]. Theoretical studies have shown that this interaction is strong in collisions of main-

group non- $S$ -state atoms, Sr( $P$ ), Ca( $P$ ), and O( $P$ ) [7,8], yielding  $\gamma \sim 1$ . Molecular beam experiments with O and Cl( $3s^23p^5\ ^2P$ ) at high temperatures ( $10^3$  K) have also indicated a significant degree of interaction anisotropy in complexes of these atoms with He, leading one to expect  $\gamma \sim 1$  [9,10]. Several metastable non- $S$ -state atoms have been magnetically trapped [11–15]. These theoretical and experimental results have indicated that evaporative cooling of magnetically trapped non- $S$ -state atoms would generally be impossible.

We present here measurements of cold elastic and inelastic collisions of Sc( $3d4s^2\ ^2D_{3/2}$ ) and Ti( $3d^24s^2\ ^3F_2$ ) with  $^3\text{He}$  and theory demonstrating that the enhancement of  $\gamma$  is due to the presence of a filled  $s$  shell with higher energy than the  $d$  shell. While the measurements for Sc provide only a lower bound on the inelastic rate, the measurements with Ti demonstrate that inelastic collisions are highly suppressed, with  $\gamma \sim 4 \times 10^4$ . Using rigorous quantum mechanical calculations we modify recently calculated interaction potentials for Ti-He and Sc-He to demonstrate the degree of the anisotropy observed and show that it is about 200 times smaller in Ti-He than the interaction anisotropy between O( $2s^22p^4\ ^3P_2$ ) and He or in van der Waals complexes of other typical non- $S$ -state atoms with He.

The experimental procedure is as follows: Hot Sc or Ti atoms in the electronic ground state are introduced via laser ablation into a cold He buffer gas in the presence of a large magnetic field (3.8 T). The atoms translationally thermalize with the buffer gas to a temperature below 2 K, where the kinetic energy becomes comparable to the splitting between Zeeman levels. Initially, all Zeeman levels are equally populated. Subsequently, the higher energy, low-field seeking atoms relax to lower Zeeman energy levels through inelastic collisions. We define the Zeeman temperature  $T_Z$  at a particular field  $B$  by equating the ratio of the local populations of two levels,  $m_J$  and  $m_{J'}$ , to the Boltzmann factor at a temperature  $T_Z$ :

$$\frac{N_{m_J}}{N_{m_{J'}}} = \exp\left(\frac{g\mu_B(m_{J'} - m_J)B}{kT_Z}\right), \quad (1)$$

where  $g$  is the  $g$  factor for the ground state ( $g = 0.66$  for Ti and  $0.80$  for Sc),  $\mu_B$  is the Bohr magneton, and  $k$  is the Boltzmann constant. We determine the cross section for inelastic collisions by measuring the rate at which  $T_Z$  relaxes to the translational temperature of the gas.

A diagram of our apparatus is shown in Fig. 1. The experiment is housed in a cylindrical copper cell which is thermally anchored to the mixing chamber of a dilution refrigerator. The cell is filled with a  $^3\text{He}$  buffer gas at a density of  $1.6 \times 10^{16} \text{ cm}^{-3}$  and cooled to an initial temperature of 350 mK.

Sc or Ti atoms are produced via laser ablation of elemental metal targets mounted at the top of the cell. The ablation is performed with a focused 15 mJ, 5 ns pulse from a frequency doubled Nd:YAG laser. The atoms are detected using laser absorption spectroscopy, on the  $^3F_2 \rightarrow ^3D_1$  transition at 395 nm for Sc, and the  $^2D_{3/2} \rightarrow ^2F_{5/2}$  transition at 391 nm for Ti. Probe powers of  $\sim 0.1 \mu\text{W}$  are typically used. It is verified that optical pumping effects are negligible.

The cell is surrounded by a superconducting magnet consisting of two coils arranged in an anti-Helmholtz configuration. This produces a spherical quadrupole field (Fig. 1). The field is zero at the center of the cell, and increases in the  $z$  direction to two saddle points near the top and bottom of the cell. The field at the saddles is 3.8 T. Zeeman level shifts in the inhomogeneous magnetic field are the dominant broadening mechanism for the absorption spectra. Atoms near the saddle points, where the field is relatively flat, provide a prominent spectroscopic peak. All of the inelastic collision data presented in this Letter are from these saddle regions.

We determine the diffusion cross section  $\sigma_d$  for Ti-He and Sc-He collisions by measuring the diffusion of Ti and Sc atoms through the helium buffer gas at zero magnetic field [16]. The diffusion cross section is a measure of the

forward momentum loss of the atoms as they diffuse through the buffer gas, and is equal to the elastic cross section  $\sigma_e$  for isotropic scattering. For Sc and Ti,  $\sigma_e \approx 2.5\sigma_d$ . The fitted diffusion times yield elastic cross sections of  $(3.1 \pm 1.4) \times 10^{-14} \text{ cm}^2$  for Sc-He and  $(3.6 \pm 1.5) \times 10^{-14} \text{ cm}^2$  for Ti-He collisions at 0.8 K.

The translational temperature of the atoms is found by fitting a Voigt profile to Sc spectra taken at zero magnetic field (Fig. 2). The previously unknown hyperfine magnetic dipole coupling constant,  $A = (169.7 \pm 1.5) \text{ MHz}$ , for the  $^2F_{5/2}$  level is determined from these spectra.

The measured translational temperature is shown in Fig. 3. Although we are unable to directly measure the Ti translational temperature at early times ( $t < 40 \text{ ms}$ , due to technical limitations of the Ti:sapphire ring laser used for Ti detection), it can be inferred from the direct measurements of the Sc translational temperature taken under identical conditions.

Inelastic collision measurements are taken at a field of 3.8 T. We monitor the populations of the low-field-seeking ( $m_j = 2$  for Ti or  $m_j = 3/2$  for Sc) and high-field-seeking ( $m_j = -2$  for Ti or  $m_j = -3/2$  for Sc) levels as a function of time, and obtain the Zeeman temperature at each time point using Eq. (1).

As shown in Fig. 3, the Zeeman and translational temperatures of Sc merge already at 2 ms, indicating a lower limit on the Sc-He inelastic collision rate of  $\Gamma_{\text{in}} > 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ , or  $\gamma < (1.6 \pm 0.3) \times 10^4$ .

For Ti,  $T_Z$  is initially much higher than the translational temperature. The Zeeman level populations thermalize to the translational temperature over tens of milliseconds. We fit the observed exponential decay of atoms in the low-field-seeking  $m_j = 2$  state over this time period to obtain the inelastic decay time  $\tau_{\text{in}}$ . We use the

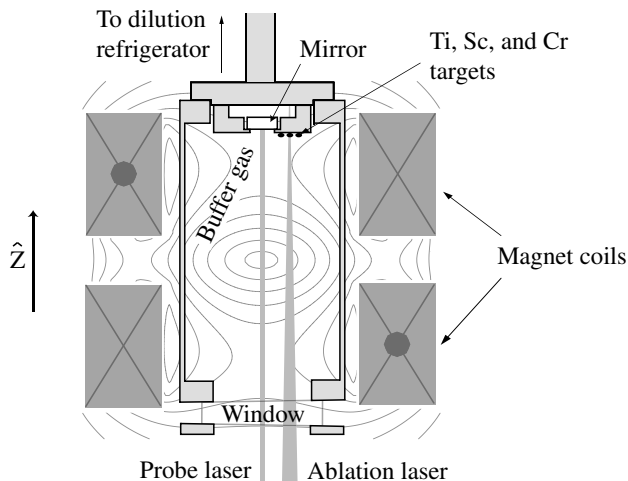


FIG. 1. Schematic of the experimental cell. Field contours are plotted every 0.6 T.

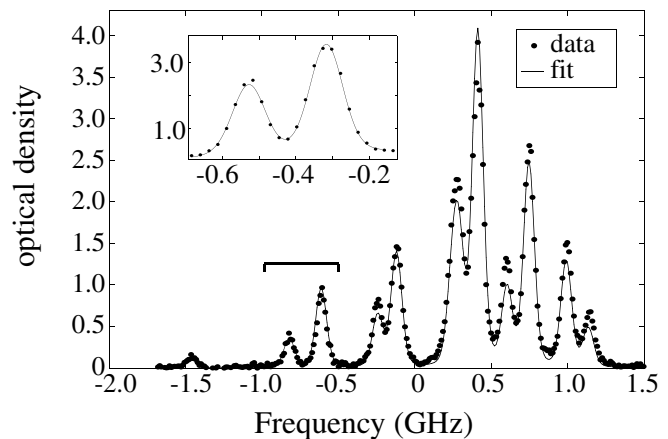


FIG. 2. Absorption spectrum of  $^{45}\text{Sc}$  ( $I = 7/2$ ) taken at zero magnetic field. The inset shows an example absorption spectrum scanning over the two hyperfine peaks indicated, taken 20 ms after the ablation pulse. Fitting the peaks with a Voigt profile yields a temperature  $T = 1.5 \pm 0.5 \text{ K}$ . Each plot has an arbitrary frequency offset.

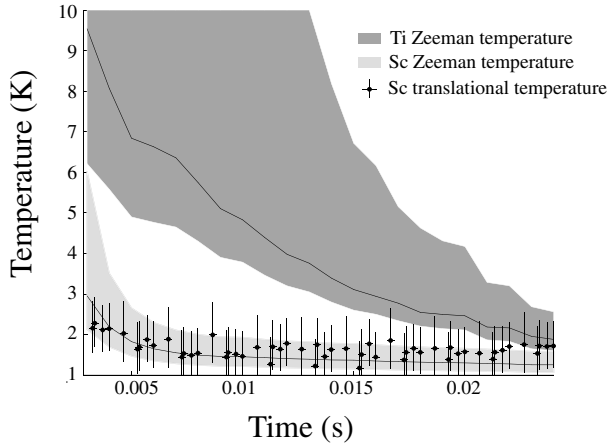


FIG. 3. Zeeman and translational temperature comparison for Ti, Sc. The ablation laser fires at  $t = 0$ . The solid lines represent the value of the Zeeman temperatures found from averaging many measurements of the high- and low-field-seeking populations. The shaded regions indicate the error bars of the Zeeman temperature measurements, mostly due to systematic errors.

measured buffer gas density  $n_{\text{He}}$  to find the inelastic collision rate constant,  $\Gamma_{\text{in}} = (\tau_{\text{in}} n_{\text{He}})^{-1}$ . At 1.8 K,  $\Gamma_{\text{in}} = (1.1 \pm 0.7) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  giving  $\gamma = (4.0 \pm 1.8) \times 10^4$ .

The energy levels of  $\text{Ti}(^3F)$  are split by interaction with He into four molecular states of  $\Sigma$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  symmetry. The dynamics of Ti-He collisions involves all four potentials and in the Born-Oppenheimer representation collisionally induced Zeeman relaxation of Ti is a nonadiabatic process. An alternative view of Ti-He collisions is based on the definition of an effective potential as a function of the interatomic separation  $R$  and the angle between the vector  $R$  and the vector describing the angular momentum of electrons in the open-shell atom [17–19]. The effective potential can be separated into an isotropic and an anisotropic part and the collision problem of Ti with He becomes equivalent to that of a  $\Sigma$  state diatomic molecule with a structureless atom. The Born-Oppenheimer description and the effective potential model can be related to show that the isotropic part of the electronic interaction is a linear combination of the  $\Sigma$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  potentials, while the interaction anisotropy is determined by the splitting between potentials of different symmetry [1,18].

Angular momentum transfer is induced in atomic collisions by the interaction anisotropy; therefore, our measurement of  $\gamma$  directly probes the splitting between the Born-Oppenheimer potentials at long range and in the vicinity of the van der Waals minimum. Recent calculations of the interaction potentials for the Ti-He and Sc-He molecules demonstrated that the potentials of different symmetry are very close in energy at interatomic dis-

tances larger than  $9a_0$  (this distance corresponds approximately to the classical turning point in Sc-He or Ti-He collisions at 2 K) [20]. The splitting between the potentials was, however, smaller than accuracy of the *ab initio* calculations and a quantum mechanical analysis could only yield an approximate value of  $\gamma$  for Sc-He and Ti-He. To estimate the degree of the anisotropy in Ti-He interactions, we simulate the experimentally measured value for  $\gamma$  by scaling the interaction potentials of Ref. [20] to decrease uniformly the interaction anisotropy in rigorous quantum mechanical calculations. This results in empirical interaction potentials that reproduce exactly the experimental value of  $\gamma$ . The calculations are performed as described earlier [8]. The interaction anisotropy near the van der Waals minimum can be characterized by the difference in binding energy of different electronic states (Table I). The binding energy difference in the Ti-He complex is several orders of magnitude smaller than that in van der Waals molecules with main-group elements.

It is interesting to compare the anisotropy of the Ti-He and Sc-He interaction derived from our calculation with

TABLE I. The absolute magnitude of the difference in the binding energy  $\Delta D$  of the different electronic states for various open-shell atom-He complexes, representing the anisotropy of electronic interaction near the van der Waals minimum. Shell type specifies whether the atom is nonsubmerged shell (NS) or submerged shell (S).

Atom	Shell type	$\Delta D(\text{cm}^{-1})$	Reference
$\text{C}(^3P)$	NS	$D_{\Sigma} - D_{\Pi} = 25.31$	Theory [21]
$\text{O}(^3P)$	NS	$D_{\Sigma} - D_{\Pi} = 11.51$	Theory [22]
$\text{O}(^3P)$	NS	$D_{\Sigma} - D_{\Pi} = 13.70$	Expt. [9] <sup>a</sup>
$\text{Al}(^2P)$	NS	$D_{\Sigma} - D_{\Pi} = 15.74$	Theory [21]
$\text{S}(^3P)$	NS	$D_{\Sigma} - D_{\Pi} = 9.37$	Theory [21]
$\text{Cl}(^2P)$	NS	$D_{\Sigma} - D_{\Pi} = 13.83$	Theory [23]
$\text{Cl}(^2P)$	NS	$D_{\Sigma} - D_{\Pi} = 5.27$	Expt. [10] <sup>a</sup>
$\text{Ga}(^2P)$	NS	$D_{\Sigma} - D_{\Pi} = 24.87$	Theory [21]
$\text{Se}(^3P)$	NS	$D_{\Sigma} - D_{\Pi} = 8.69$	Theory [21]
$\text{Ti}^{2+}(^3F)$	NS	$D_{\Phi} - D_{\Delta} = 945$	Theory [24]
$\text{Ti}^{2+}(^3F)$	NS	$D_{\Phi} - D_{\Pi} = 340$	Theory [24]
$\text{Sc}^{2+}(^2D)$	NS	$D_{\Delta} - D_{\Sigma} = 1250$	Theory [24]
$\text{Sc}^{2+}(^2D)$	NS	$D_{\Delta} - D_{\Pi} = 140$	Theory [24]
$\text{Sc}(^2D)$	S	$D_{\Sigma} - D_{\Pi} = 0.05$	Theory [20]
$\text{Sc}(^2D)$	S	$D_{\Sigma} - D_{\Delta} = 0.24$	Theory [20]
$\text{Sc}(^2D)$	S	$D_{\Sigma} - D_{\Pi} > 0.013$	Expt. (this Letter)
$\text{Sc}(^2D)$	S	$D_{\Sigma} - D_{\Delta} > 0.065$	Expt. (this Letter)
$\text{Ti}(^3F)$	S	$D_{\Sigma} - D_{\Pi} = 0.138$	Theory [20]
$\text{Ti}(^3F)$	S	$D_{\Sigma} - D_{\Delta} = 0.120$	Theory [20]
$\text{Ti}(^3F)$	S	$D_{\Sigma} - D_{\Phi} = 0.187$	Theory [20]
$\text{Ti}(^3F)$	S	$D_{\Sigma} - D_{\Pi} = 0.056$	Expt. (this Letter)
$\text{Ti}(^3F)$	S	$D_{\Sigma} - D_{\Delta} = 0.049$	Expt. (this Letter)
$\text{Ti}(^3F)$	S	$D_{\Sigma} - D_{\Phi} = 0.077$	Expt. (this Letter)

<sup>a</sup>Measurements performed by glory analysis in a molecular beam at  $T \sim 10^3$  K.

that in doubly ionized  $\text{Ti}^{2+}$ -He and  $\text{Sc}^{2+}$ -He complexes [24]. The double ionization of the Ti or Sc atom removes the outer  $s$ -shell electrons. The significant magnitude of the binding energy in the charged complexes is determined by the charge-induced-dipole interaction, hybridization of atomic orbitals affecting the repulsive part of the interaction [25], and the dispersion interaction. The induction interaction is determined by the charge of the transition metal ion and the polarizability of He so it is isotropic. The large interaction anisotropy in  $\text{Ti}^{2+}$ -He and  $\text{Sc}^{2+}$ -He ions is due to the dispersion interaction and the specific structure of the transition metal ions allowing for the  $sd_\sigma$  hybridization which may reduce occupation of the antibonding orbitals [24,25]. The comparison of the binding energy differences in the Ti-He and Sc-He complexes with those in the doubly ionized complexes thus confirms our hypothesis that the interaction anisotropy suppression in Ti-He and Sc-He is due to the outer filled  $s$  shell.

Summarizing our theory result, we have derived empirical potentials for  $\text{Ti}(^3F)$ -He and  $\text{Sc}(^2D)$ -He interactions by fitting the experimental values of the elastic-to-inelastic ratios. This calculation maps the measured data onto the Born-Oppenheimer picture of the transition metal-He interaction and provides a quantitative measure of the interaction anisotropy in the Ti-He and Sc-He complexes. The comparison of the derived interaction anisotropy with available data for the interaction anisotropy of main-group non- $S$ -state atoms, and the  $\text{Ti}^{2+}$ -He and  $\text{Sc}^{2+}$ -He complexes, elucidates the role of the filled outer  $s$  shell in determining interatomic interactions.

In conclusion, we have measured the Zeeman relaxation rate in cold collisions of  $\text{Ti}(3d^24s^23F_2)$  with He and found that the inelastic transitions are highly suppressed. It is shown that the anisotropy of the electrostatic interaction between Ti and He is very small. This suggests that the polarizability of the Ti atom is nearly isotropic and angular momentum transfer in Ti-Ti collisions must be also suppressed. This is encouraging evidence that evaporative cooling of Ti and other submerged shell atoms to the ultracold regime may be possible. If so, the scope of ultracold atomic physics would be increased to include submerged shell transition metal atoms and, perhaps, all submerged shell atoms, which account for over a third of all atomic species in the periodic table.

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