

## Relation between magnetic and structural anisotropy in the $\text{Ni}_{23}\text{Se}_{12}(\text{PET}_3)_{13}$ cluster compound

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We have measured the magnetic properties of the cluster compound  $\text{Ni}_{23}\text{Se}_{12}(\text{PET}_3)_{13}$ , where  $\text{PET}_3$  is triethyl phosphine, by dc magnetization (1.5–300 K) and ac susceptibility (0.280–4 K). We observe a small, almost temperature-independent, magnetic moment of only  $\sim 2\mu_B/\text{cluster}$  indicating the presence of two unpaired spins in the cluster. Despite the large shape anisotropy of the molecule, we find no preferred magnetic axis. We interpret this as the result of delocalization of the valence electrons due to covalent Ni-Se bonding.

### INTRODUCTION

The study of magnetic materials has intensified due to their tremendous importance in modern technologies. Many new efforts have focused on the effects of system size on magnetic properties.<sup>1–4</sup> As the physical dimensions that characterize the magnetism of a material shrink, one expects the onset of quantum-mechanical effects. In addition to providing testbeds for theories of basic phenomena,<sup>2,5</sup> these effects may be useful in future storage media and, perhaps, in other applications such as magnetocaloric cooling.<sup>6</sup> These ideas have already borne fruit in advances in magnetic films (two-dimensional systems)<sup>7</sup> and there is now great interest in the synthesis and characterization of small particles, confined in three dimensions.<sup>3</sup> The technological goal is a compound which

can exist in distinct magnetic states and which can be converted reversibly from one state to another by an external input (bistability).

Size-confinement has often been achieved by applying lithographic techniques to reducing the feature size of bulk materials.<sup>2</sup> A complementary approach, which has been attempted more recently, is to build systems “from the ground up” using metallo-organic compounds as building blocks.<sup>8</sup> These materials allow a test of the fundamental limits of magnetic domain size by two universal phenomena: quantum tunneling and thermal fluctuations. Both phenomena have been observed in small domain-size compounds at low temperature ( $< 5$  K).<sup>2,4,5</sup> In this article, we focus on a third limitation: the lack of magnetic anisotropy in covalently bonded systems.

Advances in synthetic chemistry have made possible

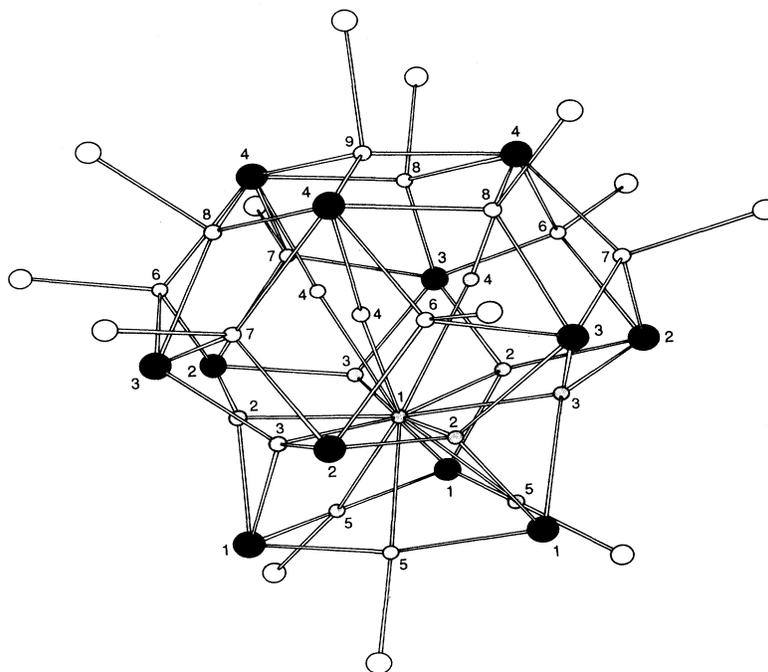


FIG. 1. Structure of a  $\text{Ni}_{23}\text{Se}_{12}(\text{PET}_3)_{13}$  cluster as determined by single-crystal x-ray diffraction. The small open circles represent Ni atoms, the filled circles Se, and the open large circle the  $\text{PET}_3$ . The lines are for clarification only and do not represent bonds.

the preparation of size-selected and monodisperse metal-chalcogenide molecules which are fragments of their respective extended lattices. This level of sample control is essential to the study of size-dependent magnetic phenomena. In this paper, we report on the magnetic properties of the  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  molecule which is a highly distorted, anisotropic fragment of the NiSe lattice (Fig. 1). Based on its structure, we expected to find a large magnetic anisotropy leading to bistability at moderate (few K) temperatures, however, this material is magnetically isotropic and follows the Curie-Weiss law from 300 K to 280 mK, showing neither bistability nor hysteresis. This is in contrast to reports of bistability in a manganese oxide cluster.<sup>4</sup> Despite its unusual shape, the anisotropy fields in this molecule are weak and there is no preferred magnetic axis. We believe these markedly different behaviors in magnetic anisotropy and moment formation are due to differences in chemical bonding (ionic vs covalent) between the two materials.

### EXPERIMENTAL METHODS

We prepared samples of  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  according to the procedures in Ref. 9 and measured dc magnetization of the material on a Quantum Design superconducting quantum interference device magnetometer. The samples are contained in an evacuated and sealed glass ampoule to prevent oxidation of this air-sensitive compound. The phosphine capping groups are weak-field ligands and prevent aggregation of neighboring clusters. Temperatures from 1.7 to 300 K are obtained through a flow of temperature-regulated helium gas in contact with the ampoule. Ac susceptibility measurements to 280 mK are made in an Oxford <sup>3</sup>He cryostat using a primary coil to generate a magnetic field and with two balanced second-

ary coils. The sample and coil assembly are mounted on a sapphire rod to a brass can to ensure good thermal contact. Temperatures are measured with a calibrated germanium resistance thermometer embedded in the brass can and are accurate to  $\pm 5$  mK.

### RESULTS

Figure 2 shows the temperature-dependent, powder averaged, inverse susceptibility of  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  as determined from the dc magnetization ( $1/\chi \equiv H/M$ ) under an applied field of  $H=0.1$  T. The solid line is a fit to the Curie-Weiss law ( $\chi = \chi_0 + C/T - \theta$ ) over the entire temperature range and yields a Curie constant  $C$  of 0.55 K emu/mol cluster and a Weiss constant  $\theta$  of 1.9 K.  $\chi_0$  contains all of the diamagnetic contributions and is approximately  $-5 \times 10^{-4}$  emu/mol cluster. Since the oxidation states of the Ni atoms are unknown, we have not attempted to calculate the contribution of the core to the magnetic susceptibility. Restricting the fit to the low-temperature data results in a slightly negative value of  $\theta$ . There is no measurable hysteresis; zero-field cooled and field-cooled samples yield identical magnetization curves (inset). Small deviations from Curie-Weiss behavior can be seen below 10 K. Figure 3 shows the effective magnetic moment,  $p_{\text{eff}} \equiv \sqrt{8\chi T}$ , as function of temperature. There is a small peak in the vicinity of 10 K where  $p_{\text{eff}} = 2.3 \mu_B$ . Below this temperature, the moment drops, indicating the depopulation of low-lying excited states.

The deviations observed in the magnetometry, taken together with the unusual shape of the molecule, led us to consider whether  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  would undergo an ordering at yet lower temperatures. These deviations, in conjunction with a negative Weiss constant, are consistent with a small ‘‘antiferromagnetic’’ interaction amongst the spins. Figure 4 shows the in-phase component of the ac susceptibility of a powder sample. There is no ordering down to 280 mK. The present of an ordering transition temperature would allow the determination of the exchange and the dipolar coupling strengths. We also compared the dc magnetization curves of a small sin-

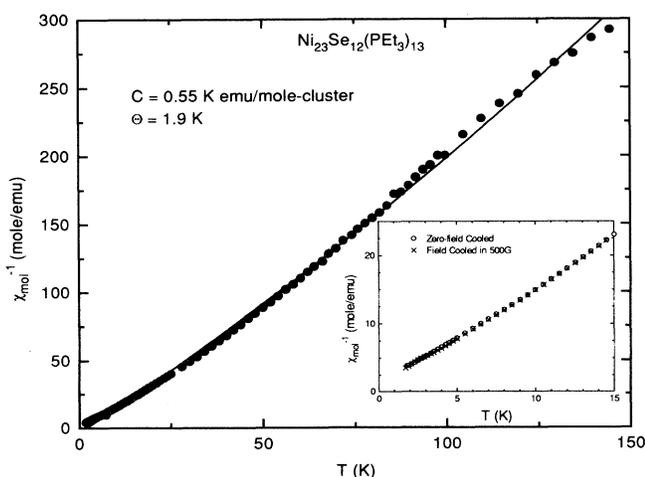


FIG. 2. Temperature dependence of the inverse magnetic susceptibility of  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  between 1.7 and 150 K measured in a field of 0.1 T. The solid line is a fit to the Curie-Weiss law over the entire temperature range;  $C=0.55$  K emu/mol cluster,  $\theta=1.9$  K. The inset shows the absence of hysteresis in magnetic properties upon cooling in zero field (open circles) and cooling in a field of 500 G (crosses).

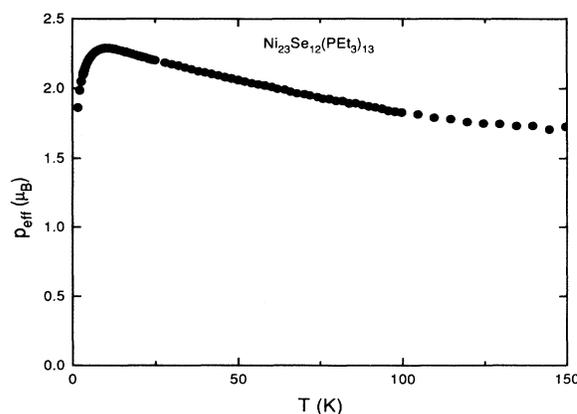


FIG. 3. The temperature dependence of the effective magnetic moment in  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$ .  $p_{\text{eff}} \equiv \sqrt{8\chi T}$ .

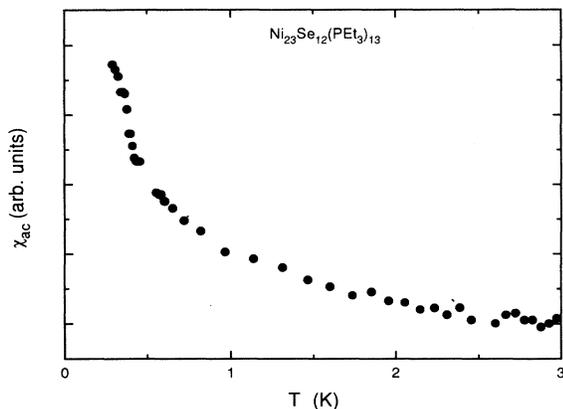


FIG. 4. Temperature dependence of the ac susceptibility of  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  between 0.3 and 3 K.

gle crystal, with its  $c$ -axis-oriented parallel to and perpendicular to the applied field and the material appears isotropic. There is, furthermore, no frequency dependence to the susceptibility. These data immediately set limits on the exchange field strengths. Any exchange interaction must be substantially lower than 280 mK. Frequency independence indicates that there are no slow relaxations. We further established that the material remains electrically insulating to the lowest temperatures.

### DISCUSSION

We note two properties of the  $\text{Ni}_{23}\text{Se}_{12}$  cluster: its magnetic moment of  $2.3\mu_B$  and its lack of magnetic anisotropy. The magnetic moment of  $0.1\mu_B$  per Ni atom is small when compared to that which could result from 23 coupled  $\text{Ni}^{2+}$  ions (as large as  $47[(46 \times 48)^{1/2}]\mu_B$ /cluster). Of course, the model of 23  $\text{Ni}^{2+}$  ions is not reasonable since there are only 12 Se atoms per molecule and therefore only 12  $\text{Ni}^{2+}$  ions could be accommodated. The observed moment is also small when compared to a 23 atom fragment of elemental Ni in which a saturation moment of roughly  $14(=23 \times 0.6)\mu_B$  would be expected. This is also flawed because there are at most 13 zero-valent (metal-like) Ni atoms in each cluster. Another possibility would be to relate the properties of the cluster with bulk NiSe systems. This is difficult since the coordination and bonding are peculiar to the molecule, even though it can be examined as a reconstructed fragment of the NiSe lattice. Rather than invoking any of these extreme models, we believe that the small magnetic moment indicates that the bonding in  $\text{Ni}_{23}\text{Se}_{12}$  is primarily covalent (as opposed to ionic) and delocalized. This behavior is similar to Ni/Te clusters studied previously.<sup>1</sup> It is therefore tempting to interpret further the magnitude and temperature behavior of the effective moment.

One rationalization is that the moment is fully local-

ized, that is, the moment is associated with electrons that are localized exclusively on particular Ni atoms. Based on the following argument we believe that this rationalization is not plausible. There are only two Ni atoms in the cluster (labeled 1 and 9 in Fig. 1) upon which a local moment could reside. The other twenty one Ni atoms are arranged by molecular symmetry into seven sets of three. The small magnitude of  $p_{\text{eff}}$  would preclude the association of the paramagnetic moment over the three Ni atoms in one of these sets. It is unlikely that a  $2.3\mu_B$  local moment resides on Ni1 because this atom looks the most like an atom of elemental nickel. It is also unlikely that a local moment would reside exclusively on Ni9 because the local coordination environment (bond distances, angles, and multiplicities) around Ni9 is the same as that around the nine atoms labeled Ni6, Ni7, and Ni8. It is thus hard to argue that the electronic structure around Ni9 is significantly different than that around the other nine cited metals.

The dependence of magnetic moment on passivating ligands has attracted recent attention. A paper by van Leeuwen *et al.*<sup>10</sup> shows that Ni moments on the surface of a  $\text{Ni}_{38}\text{Pt}_6$  cluster are strongly quenched by carbonyl groups. In our case, the triethyl phosphine groups are weak-field ligands which will not directly result in the quenching of the core moment. The magnetic properties of several small Ni/Te and Co/Te clusters capped with  $\text{PET}_3$  have been measured.<sup>1</sup> In these systems, most of the metal atoms are on the surface, yet it is clear that the phosphine groups do not quench the surface moments.

This analysis leads us to postulate that the paramagnetism of  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  is due to electrons in orbitals that are delocalized over the entire cluster (or at least over a large portion of the cluster). The Ni atoms provide the magnetic character, the Se atoms the spin-orbit coupling. The absence of magnetic anisotropy implies that the orbitals in which the "paramagnetic electrons" reside are nearly spherically symmetric. Since the center of the cluster (the thirteen Ni atoms labeled 1, 2, 3, 4, and 5) is an array that almost perfectly recapitulates a fragment of hcp elemental Ni, we believe that this interpretation of the magnetism of  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$  is reasonable.

### CONCLUSIONS

We have measured the magnetic properties of the cluster molecule  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$ . We find an unexpectedly small moment of  $\sim 2\mu_B$ /cluster, a cusp in the effective moment at approximately 10 K, and a slight deviation in the susceptibility from Curie-Weiss behavior below this temperature. No clear phase transitions are seen down to 280 mK. There are no significant intermolecular interactions and no evidence of three-dimensional ordering. We suggest that the lack of magnetic anisotropy despite the pronounced shape anisotropy of the molecule results from covalent Ni-Se bonding, resulting in a delocalized magnetic moment.

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<sup>6</sup>For example, *Chem. Eng. News* **70**, 18 (1992).

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