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A Reinterpretation of the Magnetic Properties of the Mixed-Valence (Nb^{V}/Nb^{IV}) Zintl Phase, $Cs_9Nb_2As_6$

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A new mixed-valent (Nb^{V}/Nb^{IV}) Zintl phase, $Cs_9Nb_2As_6$, has been prepared and characterized, recently (Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 5920). Niobium is present in the form of isolated, edge-sharing tetrahedral, $Nb_2As_6^{9-}$ dimers. The reported magnetic susceptibility features a broad maximum at ~36 K which has been interpreted as the onset of long-range antiferromagnetic order. Such a high transition temperature is difficult to understand as the compound is insulating and the interdimer Nb–Nb distance is 7.2 Å. It is shown here that the observed magnetic properties follow straightforwardly from a statistical occupation of the equivalent intradimer Nb sites by equal concentrations of $Nb^{IV}(4d^1, S = {}^1/_2)$ and $Nb^{V}(4d^0)$. From this analysis the broad maximum arises from intradimer antiferromagnetic exchange with an exchange constant, $J/k = -40$ K, and there is no long-range magnetic order except, possibly, below 5 K.

Introduction

In a recent report in this journal the first examples of a mixed-valence, transition metal Zintl phase were prepared and characterized, namely, $K_{38}Nb_7As_{24}$ and $Cs_9Nb_2As_6$.[1]

Both compounds feature isolated edge-sharing tetrahedral dimers, $Nb_2As_6^{n-}$. In particular the latter material, $Cs_9Nb_2As_6$, contains only dimers of the type $Nb_2As_6^{9-}$, which requires that both $Nb^{V}(4d^0, S = 0)$ and $Nb^{IV}(4d^1, S = {}^1/_2)$ are present. The Nb sites in each dimer, while not strictly equivalent, crystallographically, have nonetheless equivalent bonding environments, which is taken as evidence for delocalization of the $4d^1$ electron between the two sites with a Nb−Nb bond order of ~0.5.

In addition to the structural characterization, magnetic susceptibility data were also reported. Fits of the data above 50 K to the Curie−Weiss law confirmed the presence of one unpaired electron per dimeric unit. At lower temperatures a broad maximum was observed near ~36 K. This was interpreted as a phase transition to an antiferromagnetic state. It was also pointed out, however, that such a high transition temperature is difficult to understand given that the closest interdimer Nb−Nb separation is 7.2 Å and that the material appears to be an electrical insulator. This rules out the possibility of a long distance coupling mediated by the conduction electrons such as via the RKKY mechanism. It is the point of this short contribution to demonstrate that the observed magnetic properties follow straightforwardly from the crystal structure and the reasonable assumption that the two Nb sites per dimer are occupied statistically by $Nb^{IV}(S = {}^1/_2)$ and $Nb^{V}(S = 0)$ ions.

Experimental Section

Sample Preparation. $Cs_9Nb_2As_6$ was prepared as described in ref 1 and kindly supplied by F. Gascoin and S. C. Sevov.

Magnetic Measurements. The magnetization of a sample of mass 36 mg was measured using a Quantum Design SQUID magnetometer, MPMS, at an applied field of 5 T. The air-sensitive sample was contained in a sealed quartz tube. Data were collected in both the zero field cooled and field cooled mode over a temperature range of 1.8 K to 350 K.

Results and Discussion

The measured susceptibility is shown in Figure 1. These results are essentially the same as those reported in ref 1. The broad maximum centered at ~36 K is clearly evident.

Broad susceptibility maxima are generally associated with short range magnetic correlations rather than long range magnetic order. As this material contains well-isolated $Nb_2As_6^{9-}$ dimers, it is natural to postulate that the observed maximum results from intradimer exchange coupling. A

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(1) Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 5920.

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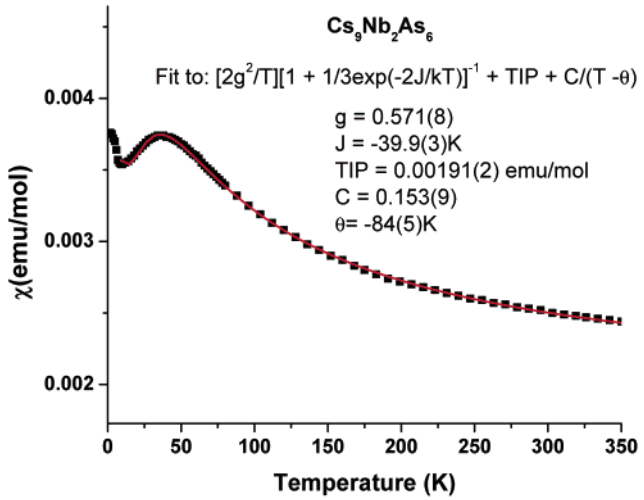

Figure 1. The magnetic susceptibility of $Cs_9Nb_2As_6$ from 1.8 K to 350 K. Only the zero field cooled data are shown, and the applied field is 5 T. The solid line is a fit to eq 1, with the parameters shown.

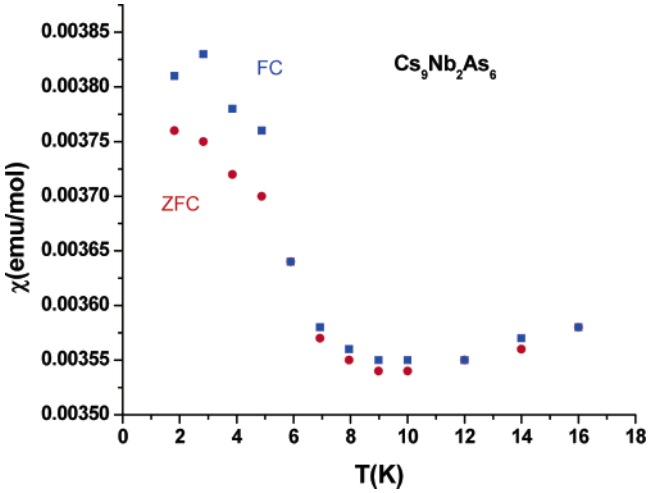

Figure 2. The magnetic susceptibility at low temperatures showing a divergence between the zero-field-cooled (ZFC) and field-cooled (FC) data below 5 K, suggesting the possible formation of a spin glassy state.

model was developed with the following assumptions: (1) that the two Nb sites within the dimer are essentially equivalent and (2) that Nb^{IV}($S = {}^1/_2$) and Nb^{V}($S = 0$) occupy these two sites with the following probabilities per dimeric unit, two $S = {}^1/_2$, 0.25, one $S = {}^1/_2$ and one $S = 0$, 0.50, and two $S = 0$, 0.25. The case with two $S = {}^1/_2$ ions per dimer can be modeled by the standard Bleaney−Bowers expression,[2] that with one ion of each spin by a Curie−Weiss law which assumes minimal interdimer coupling and the situation with two $S = 0$ will contribute at most a TIP term. The detailed model used is shown in eq 1 where the first term is the Bleaney−Bowers expression:

$$\chi_{mol} = [2g^2/T][1 + 1/3\exp(-2J/kT)]^{-1} + C/(T - \theta) + \chi_{TIP} \quad (1)$$

The data were fitted by refining the five adjustable parameters, giving the following values: $g = 0.571(8)$, $J/k = -39.9$ K, $C = 0.153(9)$, $\theta = -84(5)$ K, and $\chi_{TIP} = 0.00191(2)$ emu-K/mol. The resulting agreement is excellent as seen in Figure 1. The values of g and C are in reasonable accord with the assumptions outlined above. Nb^{IV} in a tetrahedral field should result in an e^1 configuration and a g factor near 2. Thus, for the above model, as the probability of two Nb^{IV} in the same dimer is 0.25, one expects $g = 0.50$. The spin only value of the Curie constant for $S = {}^1/_2$ is 0.375 emu-K/mol. As 50% of the Nb^{IV} ions are paramagnetic, the expected value is $C = 0.188$ emu-K/mol. These results suggest that the case of two Nb^{IV}/dimer may be slightly preferred by about 15% relative to random occupation. This is not unreasonable as the previous study suggested a weak bonding interaction within the dimer which would be enhanced in the case of double occupation by Nb^{IV}. The value for the intradimer exchange constant, $J/k = -40$ K, indicates moderate spin−spin coupling. To our knowledge there are very few model compounds for comparison and magnetochemical correlations cannot be used to understand the observed sign and magnitude. This would be an attractive case for computational study.

Thus, the magnetic properties of $Cs_9Nb_2As_6$ can be understood in terms of short range magnetic correlations, i.e., intradimer correlations and it is not necessary to invoke longer range interactions to explain the basic features of the data. Nonetheless, there is some evidence for longer range interactions from Figure 2, which shows a weak divergence between the zero field cooled and field cooled data below 5 K. Given the high degree of disorder in this material, this is likely evidence for a spin glass like state at low temperatures.

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(2) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.