CONF-731104--9

X-RAY PHOTOEMISSION STUDIES OF RARE EARTH HARD MAGNETS

J. R. Cuthill, A. J. McAlister, and N. E. Erickson
National Bureau of Standards, Gaithersburg, Md. 20760

R. E. Watson
Brookhaven National Laboratory,[†] Upton, N. Y. 11973

ABSTRACT

The present investigation attempts to probe the electronic properties of the RCO_5 compounds by x-ray photoelectron spectroscopy studies of SmCo_5 and PrCo_5 and endeavors to relate the results to the properties of the pure metals and to the picture developed to describe the magnetism of the compounds. The results indicate a valence band structure which is similar to that of Co metal; there is the suggestion that if there is charge flow it is off the rare-earth sites; there appears to be significant change in the 4f spectra from that of the pure rare-earth metals; and there is a suggestion of f-d hybridization.

INTRODUCTION

The rare-earth cobalt compounds form an interesting and valuable class of magnetic materials as is evidenced by sessions elsewhere in this conference. It would appear¹ that the magnetism is primarily associated with the Co sub-lattice, the rare-earths causing that sub-lattice to be of lower coordination than Co metal. Given the Co magnetization, the rare-earths align antiferromagnetically in its field. In the present study, x-ray photoelectron spectral data is obtained on the valence bands and pertinent inner levels in pursuit of the relationship between the magnetic behavior and the electronic structure of these compounds.

EXPERIMENTAL DETAILS

The SmCo_5 and PrCo_5 compounds were made using high-purity alumina crucibles in an induction furnace backfilled with Ti-gettered argon to a pressure of 600 torr. Reaction between the rare-earth and crucible was minimized by adding the rare-earth after melting the cobalt. The charge was held molten for two minutes after the addition of the rare-earth to insure complete reaction of the rare-earth, then poured into a chilled steel mold while still under argon. Metallographic inspection of both SmCo_5 and PrCo_5 ingots, in their as-cast condition, revealed approximately 10% of a second phase which was presumed to be R_2Co_{17} . Following Ray and

[†] Supported by USAEC.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Millott², the SmCo_5 and PrCo_5 ingots were then homogenized for 12 hours at 1220°C and 1115°C , respectively, which in each case is $\sim 115^\circ\text{C}$ below the peritectic decomposition temperature of the respective RCo_5 phase. Re-examination of the microstructure revealed that this homogenization treatment had resulted in a single phase throughout. X-ray diffraction studies confirmed the homogenization and showed the samples to have the CaCu_5 structure.

The x-ray photoelectron spectra were obtained on a modified A.E.I. spectrometer,* equipped with a P.E.I. ion gun for cleaning. The specimens were given a metallographic polish before insertion in the spectrometer and then were either argon-ion or neon-ion cleaned in situ. The cleaning was repeated at approximately 15-minute intervals. All spectra were recorded digitally at 0.2 eV intervals on a multichannel analyzer. The pressure in the specimen chamber during recording was less than 5×10^{-9} torr.

RESULTS

The core level spectra of Co in PrCo_5 and SmCo_5 are unshifted from, and are of almost identical structure and breadth, to the spectra of pure Co. As an example, the 3s spectrum of Co in SmCo_5 is compared with that of Co metal[†] in Fig. 1. There is no evidence

Fig. 1. The Co-3s spectrum.

of different spectra for the two crystallographically nonequivalent Co sites which occur in the compound, suggesting that the sites are electronically very similar. Either spectrum is a composite of lines associated with the coupling of the 3s hole with the d shell. The two spectra are almost identical, suggesting that the Co spin moment in the alloy is essentially that of Co metal, consistent with the neutron diffraction data.³

The fact that the Co spectrum does not shift on going to the alloy is not compelling evidence

against charge flow between Sm and Co sites because any chemical shift of the core level will be accompanied by a similar chemical shift of the d bands and hence of the Fermi level, ϵ_f , which falls high in the d bands. In other words there will be a tendency of the core level to be "pinned" to ϵ_f . Since photoemission measures⁴ the

*The mention of a manufacturer by name is for identification only and does not imply endorsement of the product by the government.

†After argon-ion cleaning, to be compatible with the treatment given the PrCo_5 , Sm, and SmCo_5 . No significant oxygen or carbon was detected. A narrower valence band spectrum has been obtained after baking out the Co.

position of a core level with respect to ϵ_f , only small core level shifts are expected for high density of states transition metals such as Co. The rare-earth core levels display 0-1/2eV increases in binding energy, relative to ϵ_f , in the compounds. This, taken with the trend⁵ in work function upon going from the rare-earths to Co, suggests that there may be some charge flow off the rare-earth sites. A quantitative estimate of the charge flow will not be attempted here.

The valence band region of the spectrum is displayed for PrCo_5 and Co in Fig. 2 and for SmCo_5 , Co^+ and Sm in Fig. 3. The Sm result is essentially identical to that of Baer and Busch⁶. The SmCo_5 spectrum represents a sum of scans, some of which were recorded after Ar-ion cleaning, and the remainder after Ne-ion cleaning. The structure 11-12 volts below ϵ_f is identified as due to the argon because it was not present after Ne-ion cleaning. Granted that a Co atom has approximately eight d band electrons whereas Sm or Pr have ~ 2 and that there are five times as many Co atoms, the spectrum 0-5eV below ϵ_f is presumably associated primarily with Co 3d character. The band widths of both compounds are about the same as that of pure Co metal. One would expect that the unhybridized Co site 3d bands would be markedly narrower in the compound because, while Co-Co distances are about the same, the number of Co-Co near neighbors is 2/3 and 3/4 (for the two types of Co sites) that of the pure metal. Band width is expected to be proportional to the number of near neighbors in a tight binding scheme for an ordered compound. Whether rare-earth-cobalt hybridization is responsible for the lack of narrowing remains to be seen⁷, but there appears to be some evidence of hybridization. Baer and Busch⁶ obtained a single 4f line for Pr metal which lies at an energy well inside the compound's d bands as is indicated by the arrow in Fig. 2. No discernable peaking is seen in the PrCo_5 spectrum at this energy but admixture of the f level with d bands, with which it is degenerate, will smear the peak out, perhaps to the point of not being observable.

In pure Sm, the spectrum 5-10eV below ϵ_f comes from five 4f electrons whereas there are three electrons, two of them d-like, contributing to the valence (0-3eV) spectrum. In the compound, there are again five 4f electrons but there are now 48 Sm and Co valence electrons; therefore the 4f spectra is expected to be less pronounced than in Sm metal. Depending on what one assumes is the background under the 5-10eV region of the compound's spectrum, the "4f" intensity is consistent (or perhaps too low) with respect to the drop in 4f count relative to the band electrons. The important feature is that the structure of the 5-10eV region is significantly different from that of pure Sm. The structure and relative intensities of the spectra of pure Sm and the other rare-earth metals have been shown^{6,8} to be associated with the various $4f^{n-1}$ final multiplet states⁹ accessible by excitations of a 4f electron out of the Hund's rule $4f^n$ ground state. The 4f shell of Sm in SmCo_5 may not be in such a ground state; the magnetic moment attributed¹⁰ to the shell is consistent with such a situation. The PrCo_5 results shed little light on this matter. The situation concerning the 4f shell is best tested by obtaining spectra of other RCO_5 compounds and it is our intent to do so.

Fig. 2. Valence band region. Arrow locates position of 4f peak in spectrum of pure praseodymium as determined by Baer and Busch.⁶

Fig. 3. Valence band region. The error bars on the SmCo_5 spectrum represent the locations of the data points and the size of the random counting error in the critical region of the spectrum discussed in the text.

ACKNOWLEDGEMENTS

The authors are indebted to D. P. Fickle for making the compounds, to C. H. Brady for the metallographic studies, and to C. J. Bechtoldt for the x-ray diffraction analyses. The authors especially wish to thank L. H. Bennett for many stimulating discussions. We also appreciate communications from F. J. Arlinghaus, C. K. Jørgensen, and Y. Baer.

REFERENCES

1. E. A. Nesbitt and J. E. Wernick, Rare Earth Permanent Magnets (Academic Press, New York, 1973).
2. A. E. Ray and H. Millott, IEEE Trans., Mag-7, 432 (1971).
3. R. Lemaire, Cobalt 32, 132 (1966).
4. See for instance R. E. Watson, J. Hudis, and M. L. Perlman, Phys. Rev. B4, 4139 (1971).
5. D. E. Eastman, Phys. Rev. B2, 1 (1970).
6. Y. Baer and G. Busch, Phys. Rev. Letters 31, 35 (1973), and to be published.
7. The band calculation of F. J. Arlinghaus (private communication) may shed light on this.
8. Y. Cox, Y. Baer, and C. K. Jørgensen, submitted to Chem. Phys. Letters, and references therein.
9. These final states are probably screened, see J. E. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B6, 1913 (1972); this is important to the position of the 4f spectrum but not to its structure.
10. See Fig. 3.2 of Ref. 1.