

Ferromagnetism of CrBe₁₂

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(Received 5 February 1968)

The intermetallic compound CrBe₁₂ has been found to be ferromagnetic at low temperatures. The ferromagnetic and paramagnetic Curie temperatures are each about 50°K, and at 1.4°K the saturation moment is approximately 0.2 Bohr magnetons per chromium atom. In the liquid-nitrogen temperature range, the magnetization follows a Curie-Weiss law with an effective magneton number of 2.22 Bohr magnetons per chromium atom. The experimental results are discussed in relation to possible magnetization schemes, and compared with other ferromagnetic intermetallic compounds. The compounds Nb₂Be₁₇, NbBe₁₂, Ta₂Be₁₇, TaBe₁₂, MnBe₁₂, UBe₁₃, MoBe₁₂, ZrBe₁₃, and CaBe₁₃ were found to be nonmagnetic and nonsuperconducting above 1.4°K.

I. INTRODUCTION

BERYLLIUM forms intermetallic compounds with a large number of metallic elements. The electronic structure of the beryllium atom is simple (only four *s* electrons), and the metallic band structure is well characterized theoretically.^{1,2} It might therefore be hoped that the electronic structure of the beryllide compounds will prove amenable to theoretical calculation and that measurements on these intermetallic compounds will provide insight into the nature of metallic properties in general. In addition, beryllium and the beryllide compounds are also interesting, since ferromagnetism, superconductivity, and normal diamagnetic behavior occur.³⁻⁷ In the present study we have concerned ourselves primarily with compounds of the form Be₁₂X, Be₁₃X, and Be₁₇X₂, where X is a metallic atom. These samples were examined both for superconductivity and ferromagnetism. We found the compound CrBe₁₂ ferromagnetic at low temperatures. This was rather surprising since chromium compounds are usually antiferromagnetic.⁸ Apart from the alloys of chromium with iron, cobalt, and nickel, where the chromium serves to decrease the moment of the magnetic element, the only ferromagnetic intermetallic chromium compounds are CrTe and Cr₃Pt₇.⁸ The occurrence of ferromagnetism in a beryllide is also of interest, since the other ferromagnetic beryllides are the compounds with iron (FeBe₂, FeBe₅).⁹ The magnetic properties of CrBe₁₂ are similar to those of the "itinerant" ferromagnets which have been investigated re-

cently.¹⁰ These details are discussed more fully in a later section.

II. EXPERIMENTAL DETAILS

A. Sample

The CrBe₁₂ sample was supplied in a shape resembling a top hat, as shown in the picture in Fig. 1. The diameters and lengths of each cylindrical section, respectively, are: top, 0.50×0.41 in.; bottom, 0.75×0.14 in. Since the sample was on loan, it was examined in this shape. The CrBe₁₂ and a number of other beryllide samples were provided by the Brush Beryllium Corp.

B. Sample Characterization

The samples were prepared by sintering approximately -200 mesh powder. Volumetric density measurements indicate that the CrBe₁₂ sample has at least 95% of the x-ray density.¹¹ The other samples appear similar. Structures and lattice parameters of the CrBe₁₂ and MnBe₁₂ samples were determined by x-ray diffractometry. The CrBe₁₂ sample had the expected Mn₁₂Th tetragonal structure with lattice parameters $a=7.235\pm 0.002$ Å, $c=4.177\pm 0.001$ Å, which may be compared with values from Pearson¹¹ of 7.23 and 4.173 Å, respectively. The MnBe₁₂ sample was not found to have the expected Mn₁₂Th structure, but gave a pattern typical of the Cu₂Mg-type structure, which is a cubic Laves phase. The lattice constant is 5.890 ± 0.004 Å. Although this structure does not accommodate MnBe₁₂ without vacancies, it has been reported to occur in a composition range MnBe₃₋₁₃.¹¹ In both samples no extra lines were found, indicating that any secondary phase must occupy less than 10% by volume of the sample.

The CrBe₁₂ and MnBe₁₂ were examined by spark spectrography. The significant impurities and the analysis of the starting beryllium are included in Table I.

¹⁰ See references for Table II.

¹¹ W. B. Pearson, *A Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pergamon Press, Oxford, 1967).

¹ T. L. Loucks and P. H. Cutler, *Phys. Rev.* **133**, A819 (1964).

² J. H. Terrell, *Phys. Rev.* **149**, 526 (1966).

³ Haruo Saji, Tokio Yamadaya, and Mitsuru Asanuma, *J. Phys. Soc. Japan* **21**, 255 (1966).

⁴ R. L. Falge, Jr., *Phys. Letters* **24A**, 579 (1967).

⁵ E. Bucher and C. Palmy, *Phys. Letters* **24A**, 340 (1967).

⁶ C. E. Olsen, B. T. Matthias, and H. H. Hill, *Z. Physik* **200**, 7 (1967).

⁷ N. E. Alekseevskii and N. N. Mikhailov, *Zh. Eksperim. i Teor. Fiz.* **43**, 2110 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 1493 (1963)].

⁸ Landolt Börnstein, *Magnetic Properties I* (Springer-Verlag, Berlin, 1962), Vol. II, Chap. 9.

⁹ A. Herr and A. J. P. Meyer, *Compt. Rend.* **265**, 1165 (1967).

TABLE I. Sample analysis.

BeO 1-1.5%	Typical analysis of starting beryllium (As provided by the Brush Beryllium Corp.) (ppm except for BeO)						Ti 100-200
	Fe 800-1200	Ni 100	Cr 100	Mn 100	Al 600-800	Si 200-400	
Significant impurities in CrBe ₁₂ sample from spectral analysis (wt.%)							
Al 0.01	Cu 0.001	Fe 0.1	Mn 0.001	Ni 0.01	Si 0.01	Ti 0.01	
Significant impurities in MnBe ₁₂ sample from spectral analysis (wt%)							
Al 0.1	Cr 0.001	Fe 0.1	Ni 0.01	Si 0.01	Cu 0.001		

C. Apparatus

The magnetic moments of each sample were determined by displacing the sample between the centers of two opposing pick-up coils. These coils were in the center of the magnetic field produced by a solenoid immersed in liquid nitrogen. This field was constant in time, but varied over the range of sample displacement by $\pm 0.4\%$. The axial field of the solenoid was calibrated using the proton magnetic resonance in paraffin oil. The opposed pick-up coils were in series with an external fixed mutual inductor, variable resistor, and shunted ballistic galvanometer. The variable resistance changed the sensitivity of the system. The sensitivity was determined by initiating or interrupting the current through the primary of the fixed mutual inductance. In order to calibrate the system, a sample of potassium chromium alum $[\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ was made into the same shape as the CrBe₁₂. The galvanometer deflection that resulted from displacing this sample was found as a function of the applied field, temperature, and sensitivity. This calibration was made in the liquid-helium temperature range, taking the molar susceptibility of the chrome alum to be $\chi_m = 1.86/(T - 0.015^\circ\text{K})$ emu/Oe.

The moment measuring system was used in liquid helium, down to 1.38°, as well as in liquid nitrogen. Intermediate temperatures were achieved when the sample warmed, after the liquid helium had evaporated. In this intermediate range, a $\frac{1}{10}$ -W, 10- Ω Allen-Bradley resistor was used as the thermometer. The formula of Clement,¹² $(\log R)/T = a + b \log R$, was used to correlate the resistance R and temperature T . The constants a and b were determined both in the liquid-helium and liquid-nitrogen boiling ranges. The two resulting R -versus- T curves were made to join by making a and b slightly temperature-dependent.

III. RESULTS

A. Ferromagnetic Moment

Measurements of the magnetic moment M of the CrBe₁₂ sample were made at liquid-helium temperatures

¹² J. R. Clement, *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corp., New York, 1955), Vol. II, p. 382.

as a function of the applied field H . Figure 1 shows the initial magnetization curve for CrBe₁₂ at 4.2°K as well as the hysteresis curve that was observed. The initial magnetization curve is seen to be relatively steep, and the remanence, 783 emu/mole, is quite large compared with the saturation magnetization. Considerable hysteresis is observed, with a coercive force (applied) of 215 Oe. The magnetization curve at 1.38°K was indistinguishable from that at 4.2°K above 400 Oe. Below this field, the only change observed was a slight 3% increase in remanence.

From Fig. 1 the magnetic moment of CrBe₁₂ does not appear to saturate at the highest fields available. However, the steep initial magnetization curve indicates, at least for some crystal orientations, that saturation is achieved in a field of a few hundred Oe. Above 300 Oe the magnetic moment still increases slightly with increasing field. Accounting for this gradual increase in moment requires some knowledge of the magnetic ordering present. If the material is simply ferromagnetic, then (1) the increase in moment can be due to that portion of the material oriented in a hard direction approaching saturation at a higher field, or (2) part of the material may approach saturation more slowly due to demagnetization effects. (3) An ordering

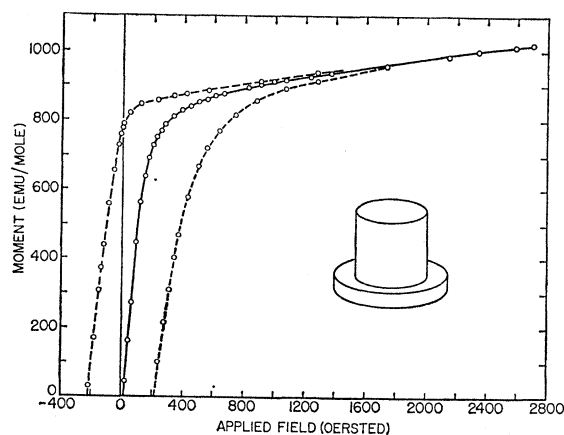


FIG. 1. Magnetization curve for CrBe₁₂. The magnetic moment per mole is plotted versus the applied field. The sample shows a marked hysteresis. The virgin curve is shown as a solid line, while the major hysteresis loop is dashed. The sample shape is depicted in the inset.

other than simple ferromagnetic may be present, with the increase in magnetization due to canting of the moments. For example, if a spiral spin arrangement were present a high field could alter the spiral structure, resulting in an increased magnetization of each domain. For reasons discussed below we do not believe explanation (2) is the appropriate one, although demagnetization effects need to be considered. If (3) is applicable, then the important experimental quantity is the spontaneous magnetization M_{sp} obtained by extrapolating the linear portion of the magnetization curve to $H=0$. M_{sp} is 810 emu/mole or $0.145\mu_B$ (μ_B is the Bohr magneton) per formula unit. If, on the other hand, the material is ferromagnetic, then the saturation moment (extrapolation to high field) is the important physical quantity. The highest moment we measured corresponded to $0.185\mu_B$ per formula unit, and on the assumption of ferromagnetism we estimate the saturation moment M_s to be about $0.2\mu_B$ per formula unit. A fourth possibility, ferrimagnetic or nearly compensated antiferromagnetic ordering, is rendered unlikely by the positive paramagnetic Curie temperature. This is discussed in Sec. IV.

B. Remanence

The remanence of the CrBe_{12} after saturation was observed as a function of temperature as the sample warmed from liquid-helium to liquid-nitrogen temperatures. This remanent moment is shown as a function of temperature in Fig. 2. The moment decreases linearly between 32 and 47°K, extrapolating to zero moment at 49.4°K. Above 47°K there is a small magnetization tail that disappears above 56°K. The Curie point is certainly above 49.4°K and is probably about 50°K.

C. Paramagnetic Susceptibility

The susceptibility (defined as M/H) was then observed in the temperature range between the triple point and normal boiling point of liquid nitrogen.

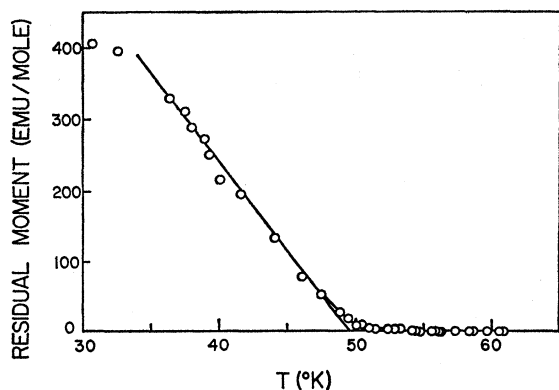


FIG. 2. Plot of the decay of the residual moment as the CrBe_{12} sample warms. First the sample is placed in a field of 2900 Oe at 4.2°K, then the field is removed. As the sample warms in zero field, its moment is always less than the spontaneous magnetization.

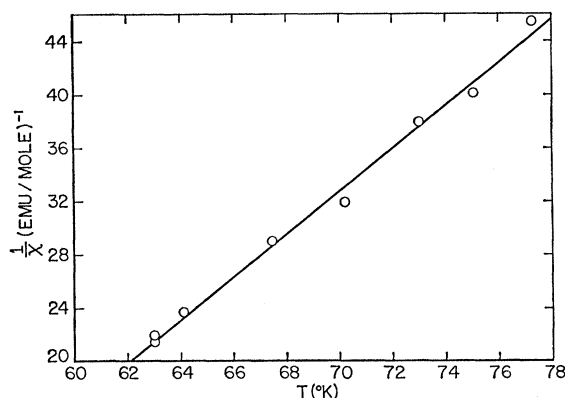


FIG. 3. Plot of the inverse susceptibility versus temperature in the paramagnetic region for CrBe_{12} .

Figure 3 shows a plot of the inverse susceptibility versus temperature, from which it is seen that the molar susceptibility χ_m of CrBe_{12} follows a Curie-Weiss law

$$\chi_m = C/(T - \theta_p) = P_{\text{eff}}^2 N \mu_B^2 / 3k(T - \theta_p) \quad (1)$$

in this temperature range with a Curie constant C of 0.619 (emu °K)/mole and a paramagnetic Curie temperature θ_p of 49.7°K. Here N is Avogadro's number and k the Boltzmann constant. The effective magneton number P_{eff} obtained from this relation is 2.22.

D. Demagnetizing Factor

In order to estimate the demagnetizing factor of our sample, moment measurements were made on a sphere of nickel (demagnetizing factor $4\pi/3$) and on a piece of nickel machined to the same shape as the CrBe_{12} sample. Comparison of the two curves allowed an effective demagnetizing factor for the hat shape to be determined. This factor was 2.5 for low fields and 3.5 for high fields for nickel. Allowing the same range of demagnetizing factors for the CrBe_{12} , we estimate that the internal field varies from 80 to 98% of the applied field. Thus the "knee" of the initial magnetization curve, which is found at $H_{\text{applied}} = 300$ Oe, corresponds to an internal field of 275 Oe, while at the highest field applied, 2707 Oe, the internal field would be 2670 Oe. These numbers are only estimates, of course, but do give the approximate magnitude of internal fields present in the sample. Since the applied field is reduced only slightly by the demagnetizing field, we do not believe the shape of the magnetization curve is due primarily to demagnetizing effects.

E. Effects of Impurities

Since iron is a fairly abundant impurity, one may wonder how much it contributes to the observed moment. The approximate quantity of iron in the sample is 0.1% by weight or 0.04 at.%, while the Cr in CrBe_{12} is 7.7 at.%. In spark-analytical work a factor of 3

TABLE II. Magnetic parameters.

Ref.	Material	Curie point θ_f (°K)	θ_p (°K)	Magneton no. P_{eff}	Saturation moment per formula unit M_s	Structure
a	Ni	631	650	1.61	0.60	fcc
b, c	ZrZn ₂	30	35	1.34	0.10-0.13	cubic Cu ₂ Mg
d	Sc ₃ In	6	8	1.30	0.16	hexagonal Ni ₃ Sn
e, f	Au ₄ V	43-51	39	1.49	0.41	tetragonal MoNi ₄
g	CrBr ₃	37	47	3.84	2.87	hexagonal
a	CrTe	333	330	4.08	2.15	monoclinic (?); hexagonal (?)
h, i	Cr ⁺⁺⁺	3.85	3.00	...
	CrBe ₁₂	~50	49.7	2.22	0.193	tetragonal Mn ₁₂ Th

^a Reference 8.

^b H. J. Blythe, Phys. Letters 21, 144 (1966).

^c R. L. Falge, Jr., and R. A. Hein, Phys. Rev. 148, 940 (1966).

^d B. T. Matthias *et al.*, Phys. Rev. Letters 7, 7 (1961).

^e L. Creveling, H. L. Luo, and G. S. Knapp, Phys. Rev. Letters 18, 851 (1967).

^f H. L. Luo, L. Creveling, and J. P. Maita, Phys. Letters 25A, 740 (1967).

^g I. Tsubokawa, J. Phys. Soc. Japan 15, 1664 (1960).

^h H. M. Rosenberg, *Low Temperature Solid State Physics* (Oxford University Press, London, 1963), p. 295.

ⁱ W. E. Henry, Phys. Rev. 88, 559 (1952).

error is not unusual, so the question of the contribution of iron should be considered. To settle this matter, an arc-melted sample of FeBe₁₂ (supplied by von Batchelder¹³), which is largely composed of crystals with the Mn₁₂Th structure, has been examined, and its susceptibility is more than two orders of magnitude less than the initial susceptibility of CrBe₁₂. Mössbauer data (provided to us by L. J. Swartzendruber, National Bureau of Standards) on another iron beryllide, crystal structure unknown, but certainly containing some Mn₁₂Th structure, indicate no Fe⁵⁷ hyperfine structure at 4.2°K. We feel this argues against the possibility of antiferromagnetism in our FeBe₁₂ sample. Alloys more rich in iron have been examined.⁹ With decreasing iron content, the moment of the alloy decreases linearly, independently of the crystal structure, indicating that the compound FeBe₁₂ should have no moment. Therefore, we feel that iron impurities, unless present interstitially, should have negligible effect on the observed magnetic properties of CrBe₁₂.

F. Other Measurements

The moment of the following beryllium compounds (supplied by Brush Beryllium Corp.) was measured at 4.2 and 1.38°K: Nb₂Be₁₇, UBe₁₃, ZrBe₁₃ (see Ref. 14), CaBe₁₃, Ta₂Be₁₇, TaBe₁₂, NbBe₁₂, and MoBe₁₂. No indication of marked magnetic behavior or of superconductivity was observed. It is believed that analysis of these samples would show similar impurities to those observed in the CrBe₁₂ and MnBe₁₂. Even though iron is nonmagnetic in the Mn₁₂Th structure, it may act to change the superconducting transition temperature of these samples. This, together with the possible off-stoichiometry of the samples would argue that the nonsuperconductivity of the above listed samples at

¹³ F. W. von Batchelder and R. F. Raeuchle, Acta Cryst. 10, 648 (1957).

¹⁴ Also investigated and found nonsuperconducting by Ref. 7.

1.38°K, is approximate. It does not seem that the quantity of impurity found is sufficient to depress the transition temperature excessively unless the natural transition temperature were already quite low.

Measurements were also made on an irregular lump of MnBe₁₂ supplied by Brush Beryllium Corp. This sample had a molar susceptibility of 0.0012 emu/mole at 77°K, 0.0013 emu/mole at 63°K, 0.0026 emu/mole at 4.2°K, and 0.0031 emu/mole at 1.38°K. No retained moment was observed. Even though the sample was prepared in the same manner as the CrBe₁₂, it must be remembered that the x-ray results showed that it did not have the same crystal structure.¹⁵

IV. DISCUSSION

A. Magnetization

In Table II are collected the available data for a number of ferromagnetic materials. From this Table it appears that the saturation magnetic moment per chromium atom in CrBe₁₂ is considerably lower than that observed in other chromium salts and compounds. Thus, the ferromagnetic insulating compound CrBr₃ (2.87μ_B) and the alloy CrTe (4.08μ_B) approximate the ionic value of Cr⁺⁺⁺ obtained from measurements on paramagnetic salts (3.0μ_B). On the other hand, a

¹⁵ A MnBe₁₂ sample provided by von Batchelder contrasted markedly with the above-mentioned MnBe₁₂ sample; its susceptibility, at 4.2°K, is 0.04 to 0.05 emu/mole, and is nearly constant in field to 2500 Oe (the highest field). We attribute this difference to the different crystal structures of the two MnBe₁₂ samples. The possibility that MnBe₁₂ is antiferromagnetic has not yet been eliminated. The moments of other elements when alloyed with beryllium and possessing the Mn₁₂Th structure is a matter under current investigation. TiBe₁₂, VBe₁₂, CoBe₁₂, PdBe₁₂, and PtBe₁₂ all have susceptibilities nearly equal to that of the above-mentioned FeBe₁₂ sample at 4.2°K. These samples all showed the Mn₁₂Th structure prominently when they were examined by von Batchelder. [See R. F. Raeuchle and F. W. von Batchelder, Acta Cryst. 8, 691 (1955); F. W. von Batchelder and R. F. Raeuchle, Acta Cryst. 11, 122 (1958); and Ref. 13].

much lower moment ($0.4\mu_B$) is indicated¹⁶ for anti-ferromagnetic chromium metal from neutron diffraction experiments. The moment of about $0.2\mu_B$ per chromium atom in CrBe_{12} is much nearer to the value predicted for chromium itself from the Slater-Pauling curve¹⁷ ($0.22\mu_B/\text{atom}$). This low moment is also of the same order of magnitude as that obtained in a number of itinerant ferromagnets listed in Table II. The ratio of P_{eff} to M_s is 2.6 for Ni and 1.9 for CrTe. Much higher ratios are obtained for the itinerant ferromagnets ZrZn_2 , Sc_3In , and Au_4V . For these the respective ratios are 10.3, 8.1, and 3.6, while for CrBe_{12} P_{eff}/M_s is 11.5. There is no apparent empirical or theoretical relation between the effective magneton numbers obtained in the paramagnetic region and the low-temperature saturation moments M_s . About all that one can say is that the ratio P_{eff}/M_s of about 10 observed in CrBe_{12} can no longer be considered unusual.

B. Ordering

The positive Curie temperature indicates a positive exchange energy so that ferromagnetic coupling is expected. Also the remanence, the Curie point, and the shape of the magnetization curve are typical of ferromagnetic behavior. Since all Cr sites are crystallographically equivalent in the CrBe_{12} structure, we would expect any simple ordering scheme to be either ferromagnetic or antiferromagnetic. In view of the above we exclude the possibility of antiferromagnetism. The other possibility, already mentioned in Sec. III, is that of a canted spin array with a net ferromagnetic moment. The cell parameters of CrBe_{12} are such that the Cr sites may be thought of as occupying four interpenetrating hexagonal Bravais lattices. Since spiral spin arrays and other complex arrangements prefer hexagonal structures, such an ordering is a definite possibility.

In the above discussion we have implicitly assumed that any moment must reside on the chromium sites. It is considered unlikely that the beryllium atoms should carry a considerable magnetic moment because of the absence of d electrons in atomic beryllium. However, if the moment is nonlocalized, there could be a moment

at the beryllium sites as well (which are not all equivalent), but the present experiments shed no light on this.

V. CONCLUSION

The compound CrBe_{12} is paramagnetic above the Curie temperature (about 50°K), and has a weak ferromagnetic moment with hysteresis below that temperature. Curie-Weiss behavior is observed in the paramagnetic region at liquid-nitrogen temperatures with an effective magneton number P_{eff} of 2.22 and a θ_p of 49.7°K . Remanence is observed in the magnetic region below the Curie point and the saturation magnetization is about $0.2\mu_B$ per formula unit, in agreement with the prediction of the Slater-Pauling curve for chromium. The material is considered most likely to be ferromagnetic with considerable anisotropy.

[*Note added in proof.* The measurements of the magnetic moment have recently been extended to 60 kOe. These measurements indicate that the apparently linear increase in moment seen in Fig. 1 continues over a large range of fields before a typical approach to saturation is observed. The saturation magnetization is about 1890 emu per mole, yielding a new estimate of the saturation moment $0.34\mu_B$ per formula unit. Since this behavior of the moment cannot be explained on the basis of any realistic estimate of the demagnetization factor, we must conclude that either some canting of moments occurs in this structure, or there is a rather large anisotropy occurring in the sample. In the field range from 20 to 60 kOe, the moment is linear when plotted against the reciprocal of the magnetic field.]

The compounds $\text{Nb}_2\text{Be}_{17}$, NbBe_{12} , $\text{Ta}_2\text{Be}_{17}$, TaBe_{12} , MnBe_{12} , UBe_{13} , MoBe_{13} , ZrBe_{13} , and CaBe_{13} are not superconductors above 1.4°K . If later work shows that chemical purity is exceedingly important, this conclusion may have to be revised. Further work to determine the magnetic structure of the beryllide compounds may well prove an interesting and fruitful endeavor.

ACKNOWLEDGMENTS

The authors thank A. J. Stonehouse of Brush Beryllium Corp. for very kindly supplying many of the samples used in this investigation. We are also indebted to C. J. Bechtoldt for his determinations of the crystal structure and lattice parameters. R. L. Parke's aid in taking the data is also acknowledged.

¹⁶ R. Nathans and S. J. Pickart, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, p. 211.

¹⁷ L. Pauling, Phys. Rev. **54**, 899 (1938).